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PROCEEDING

1 - Novel methodologies for Molecular Electronic Structure
2 - Modeling and simulation of Low-dimensional systems

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Symposium-1: Novel methodologies for Molecular Electronic Structure

ADIABATIC CONNECTION METHOD FOR THE CORRELATION ENERGY OF STRONGLY CORRELATED SYSTEMS

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Keywords : dynamic correlation energy, adiabatic connection, strong correlation

Abstract: Strong correlation can be essentially captured with multireference wavefunction methods such as complete active space (CAS) or, if dozens of active electrons are involved, with density matrix renormalization group (DMRG) technique. It is known that accurate description of electronic structure of strongly correlated systems requires accounting for the dynamic electron correlation, which CAS and DMRG largely miss. Second-order perturbation corrections are used to address the problem of dynamic correlation energy but they may suffer from intruder states and lack of size consistency. They are also expensive, which precludes them from using with DMRG with very large number of active orbitals.

In my talk a new method for the correlation energy based on the adiabatic connection [1,2] will be presented. It employs the particle-hole multireference random phase approximation and a Cholesky decomposition technique. It is free from instability or intruder state problems and rigorously size-consistent. The computation cost of the method grows with the fifth power of the system size, which is unprecedentedly low comparing with other ab initio multireference dynamic correlation methods. I will show that the method combined with CASSCF and DMRG and applied to singlet and triplet states of organic biradicals leads to obtaining the ST gaps with the average error below 0.1 eV [3].

This development opens new perspectives for accurate calculations of systems with dozens of strongly correlated electrons.

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QUANTUM-CLASSICAL CALCULATION OF COLLISION RATE COEFFICIENTS AND TRANSPORT PROPERTIES: LONG-RANGE INTERACTIONS AND QUANTUM EFFECTS

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Keywords : mixed quantum-classical methods, potential energy surfaces, molecular dynamics,

Abstract: The theoretical determination of many physical properties in gaseous environments or in non-equilibrium plasmas relies on the accurate modelling of collisional elementary processes, whose basic ingredients are the characterization of the intermolecular interaction potentials and a dynamical treatment able to capture the classical and/or quantum nature of the scattering.

A classical behavior is generally assumed for the dynamical evolution of the colliding particles. Nonetheless, the quantum behavior of some degrees of freedom plays a most relevant role at low temperature or when state-to-state quantities need to be computed. When light atoms are involved, quantum effects may determine the outcome of the process at any considered temperature. Here, the main quantum effects arising in the calculation of inelastic and reactive rate coefficients and transport collision integrals are evaluated by using mixed quantum-classical methods. In the present formulation [1-3], translational and rotational motions are treated classically whereas the vibrational motion is quantized, allowing the inclusion of the most relevant quantum effects.

Progress in computational resources and in efficient interpolation procedures has allowed to obtain fast and reliable potential energy surfaces in the region of strong interaction between the colliding partners. The medium and long-range regions, on the other hand, often remain neglected or only poorly characterized, a choice justified by the belief that only the short-range potential drives the dynamics. Increasing evidence [4,5], shows that on the contrary the outcome of collisional events is strongly influenced by the formation of weakly bound complexes or precursor states, which need to be correctly and accurately described. Therefore, the basic role of the long-range potential for the determination of physical properties ranging from the second virial coefficients to integral cross sections and rate coefficients, will also be quantitatively illustrated and discussed.

Finally, it will be shown how the proper consideration of both quantum dynamical effects and the correct description of long-range forces allows to reconcile long existing differences between experimental and calculated data.

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MULTIPLE SOLUTIONS IN ELECTRONIC STRUCTURE: EXCITED STATES, SYMMETRY BREAKING, AND STRONG CORRELATION

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Multiple solutions are an inherent feature of the electronic Schrödinger equation, representing the ground and excited states of an electronic system. The interaction between these states plays an essential role in photochemical processes throughout chemistry. However, excited states can be difficult to accurately describe using theoretical techniques. One particularly appealing approach is to search for higher-energy mathematical solutions to ground-state methods. While these state-specific approximations promise a more accurate representation of electronic excited states that can account for relaxation of the electron density, the existence and mathematical properties of these solutions remain to be fully understood.

In this talk, I will present our recent progress in understanding the properties of higher-energy solutions to the electronic Schrödinger equation. I will introduce a geometric perspective where these solutions are considered as higher-energy stationary points on a high-dimensional energy landscape. By considering the properties of the exact energy landscape, I will show that excited states form stationary saddle points and the ground state represents the unique global minimum.[1] I will then demonstrate how approximate wave functions such as the Hartree-Fock and multiconfigurational self-consistent field methods can be considered as constrained subspaces of the exact energy landscape.[2-4] This discussion will explore how the existence and properties of multiple solutions depends on the wave function flexibility and types of electron correlation in the system, highlighting the successes and failures of these methods. Finally, I will outline some of the opportunities and challenges for practical excited-state calculations.

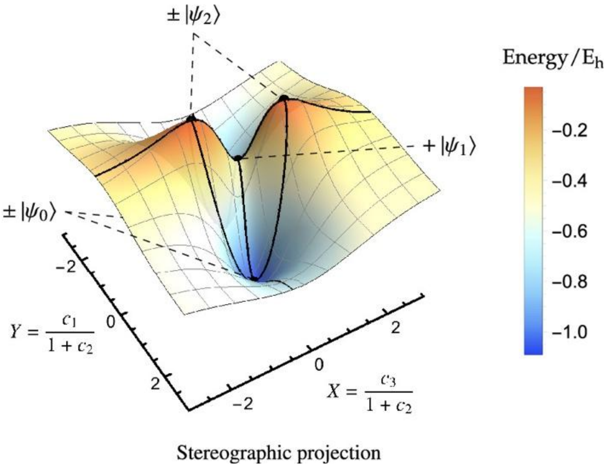

Figure 1: Exact energy landscape for singlet H_2 showing the two excited states as a saddle point and maximum of the energy.

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ANALYSIS OF RESEARCH TREND ON THE MOLECULAR INTEGRALS OVER SLATER TYPE ORBITALS

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The efficient and reliable evaluation of multicenter molecular integrals over Slater type orbitals (STOs) is one of the oldest mathematical and computational problems of molecular electronic structure theory. Through bibliometric analysis, the aim of this paper is to understand the recent research trend on the molecular integrals over STOs. And also, the present study aims to identify the most productive authors, journals, and the most used keywords on the molecular integrals over STOs. The data were collected in the Web of Science Core Collection during 1975-2021.

Key words: Slater type orbitals; Molecular integrals; Bibliometric analysis; Web of Science

NOVEL APPROACH TO THE DISSOCIATION OF CHEMICAL BOND BASED ON HIGH SECTORS OF FOCK SPACE AND MULTIREFERENCE COUPLED CLUSTER THEORY

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Keywords: multireference Fock space coupled cluster method, Intermediate Hamiltonian, potential energy curves, spectroscopic constants, alkali metal dimers

Abstract: The studies of the potential energy curves (PECs) of diatomic molecules have a well established place in the quantum chemical literature. The problem is challenging since upon the dissociation of the closed shell structure usually the open shell fragments are formed (the obvious exception are dimers of the alkali earth metals bound with the van der Waals type forces) which complicate the calculations at the correlated level. Hence, e.g. in the case of the dissociation of the alkali metal diatomics the dominant approach is based on the effective core potential (ECP) which replaces electrons of the inner shells by the model potentials and owing to that reduces the correlated calculations to two valence electrons.
Our concept - based on the first principle approach - relies on the adoption as a reference system the positively ionized structure selected in such a way that its dissociation products are the closed shell fragments. The next step - within this strategy - requires a proper version of the multireference Fock space (FS) coupled cluster (CC) approach capable to recover the original neutral structure [1,2,3].

Focusing on the PECs generated with the (2,0) and/or (3,0) sector of FS we may indicate a number of diatomics which upon removal of two or three electrons from a neutral structure dissociating into the closed shell fragments.

The precise knowledge of the interatomic potential for diatoms composed of alkali and alkaline-earth metal elements is crucial, e.g., in the design of the synthesis of molecules in the ultra-low temperatures, one of the most popular research topics in recent years and one of the fastest growing research areas. The application power of these studies is enormous, e.g., a high precision spectroscopy, quantum computers, superaccurate determination of the fundamental physical constants, the opportunity for studying chemical reactions, etc.. Currently, cold chemistry is a very promising and future-oriented branch of chemistry.

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QUANTUM SCATTERING OBSERVABLES FROM VERY ACCURATE QUANTUM CHEMISTRY CALCULATIONS

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Keywords : Potential energy surfaces, molecular interactions, cold collisions

Abstract: Recent experiments in molecular scattering at low collision energies pose a significant challenge for theory. Two main problems need to be addressed to make a stringent comparison with an experiment: the first step is the solution of the electronic Schroedinger equation; secondly, the nuclear Schroedinger equation. Both tasks are formidable, especially in the case of systems where rotational constants of molecules are small and interaction potentials of colliding species are strongly anisotropic. In the low kinetic energy regime, the quantum nature of the scattering reveals, and such phenomena as scattering resonances become pronounced[1].

In this presentation, I will discuss how the quantum phenomena can be predicted from ab-initio quantum chemistry calculations. It is not easy, as the Born-Oppenheimer potentials needed for quantum dynamics calculations should be extremely accurate, with an accuracy exceeding gold-standard CCSD(T) method. Even with high accuracy Born-Oppenheimer potential, it is still needed to account for the nuclear motion of molecules while colliding species interact. I will show how this can be addressed for a simple 4-electron system of metastable helium colliding with the hydrogen molecule [1,2,3].

I will also show the most recent studies of collisions in the Ne*+ H2 system where low-lying, narrow p-wave shape resonance was discovered. We have also achieved excellent agreement between theory and experiment for that particular system[4]. Finally, I will present a more complex system: Sr atoms interacting with the O2 molecule, which despite complexity (many electrons, heavy nuclei, open-shell molecule), quantum chemistry can give quantitative predictions for inelastic collision rates in the ultracold regime. The study presented here suggests that experimental collisional cooling of O2 atoms by ultracold Sr bath might lead to quantum degeneracy of O2 gas.

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ANALYTICAL EVALUATIONS IN INTEGRALS OF EXPONENTIALLY CORRELATED HYLLERAAS-CI WAVEFUNCTIONS

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1) Department of Chemistry, Michigan State University, East Lansing, United States

Keywords : explicit correlation, integral evaluation, beyond Gaussians, Hylleraas-CI method, Slater geminal

Abstract: A generalization of Hylleraas-CI method was introduced using Slater geminals [1]. The analytical evaluations of unlinked three- and four-electron integrals are derived. The present approach is an extension of the work from Ruiz [2]. The treatment of combining diverged integrals to obtain finite values is avoided in the present approach, as described in previous literature [3,4].

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CLOUD-COMPUTING WEB-SERVICE FOR HARTREE-FOCK METHODS

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Keywords: Hartree-Fock, Cloud Computing, Quantum Chemistry, Computational Chemistry

Abstract: We introduce an open-source cloud-based computational framework for solving the Hartree-Fock equations. Using state-of-the-art distributed software engineering tools, the software will feature a front-end web-interface and a modular implementation of an extensive set of computational methods.

Flexible software tools for Hartree-Fock calculations are hard to come by due to the highly complex nature of the problem. In our software project, we aim to provide an open-source environment with a user-friendly web-service that facilitates the use of a large number of different methods. Novelty subroutines can be easily integrated and interchanged.

The software will integrate existing state of the art methods and libraries as well as options for a variety of modifications, while ensuring ease of use for users without a programming background. As such, it is potentially attractive to practitioners who may be deterred by the steep learning curve entailed in using a highly complex software system or by the need to invest a large effort in writing code of their own.

In this novel cloud-computing environment, the solution procedure is split into several small tasks, which are distributed across the cloud service, optimized either for speed or cost. To facilitate the application of large-scale computations, we also incorporate different basis sets such as STO bases in an effective manner and plan to extend the software to become a state-of-the-art global electronic structure development environment suitable for a variety of tasks and users.

EXCITED-STATE DYNAMICS OF MOLECULAR PHOTO-SWITCHES: METHOD DEVELOPMENT AND APPLICATIONS

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Dithienylethene (DTE) molecular photoswitches have shown to be excellent candidates in the design of efficient optoelectronic devices, due to their high photoisomerization quantum yield (QY)[1], for which symmetry is suggested to play a crucial role. Here, we present a theoretical study on the photochemistry of a nonsymmetric dithienylethene photoswitch, with a special emphasis on the effect of asymmetric substitution on the photocyclization and photoreversion mechanisms. We used the Spin-Flip Time-Dependent Density Functional Theory method to locate and characterize the main structures (conical intersections and minima) of the ground state and the first two singlet excited-states, along the ring-opening/closure reaction coordinate of the photocyclization and photoreversion processes[2]. Additionally, we identified the important coordinates governing the radiationless decay pathways. Since the photoisomerization is a dynamical process, the QY of the photocyclization and photoreversion must be quantified to fully understand the effect of the asymmetry substitution. This can be achieved running a nonadiabatic molecular dynamics simulation such as the trajectory surface hopping approach developed by Tully[3]. We show the implementation of this approach and its integration into PySurf[4]. Furthermore, the photorelaxation of a set of test molecules are presented.

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BENCHMARKING GNOF AGAINST FCI IN CHALLENGING SYSTEMS IN 1-,2- AND 3-DIMENSIONS

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Keywords: Electron Correlation, Reduced Density Matrix Functional Theory (RDMFT), Natural Orbital Functional Theory (NOFT)

Abstract: Appropriate representations of the electronic structure of atoms, molecules and solids without explicit recourse to the N-particle density matrix can alternatively be obtained by the one-particle reduced density matrix (1RDM) functional theory [1]. Regrettably, computational schemes based on the exact constrained search formulation are too expensive; so the 1RDM functional requires a practical approach. For a Hamiltonian involving no more than two-body interactions, the ground-state energy can be cast as an exact functional of the two-particle reduced density matrix (2RDM). In practical applications, we employ this exact energy functional but using an approximate 2RDM that is built from the 1RDM.

Approximating the energy functional has a major consequence: the functional N-representability problem arises. In this presentation, the role of the N-representability in approximate functionals [2] will be analyzed.

The 1RDM functional is called Natural Orbital Functional (NOF) when it is based upon the spectral expansion of the 1RDM. Several approximate functionals have been proposed [3], but solely PNOFs [4,5] are based on the reconstruction of the 2RDM subject to necessary N-representability conditions. For the latter, an open source software is available [6] for quantum chemistry calculations. These functionals are capable of producing a correct description of systems with a multiconfigurational nature, however, they also suffer from an important lack of dynamic correlation. To recover this correlation, second-order perturbative corrections have been implemented with significant results [5,7]. Nevertheless, our goal is to recover the missing dynamic correlation only within the NOF theory framework.

In this talk, a new accurate NOF will be presented for all electronic structure problems, that is, a global NOF [8,9]. Note that the adjective "global" is used instead of "universal" to differentiate our approximate multipurpose NOF from the exact functional. The concept of the dynamic part of the occupation numbers will be introduced. The emergent functional describes the complete intrapair electron correlation and the correlation between orbitals that make up both the pairs and the individual electrons. The interorbital correlation is composed of static and dynamic terms. Different examples will be analyzed where the weak and strong electron correlations are revealed. Our results will be compared with those obtained by established accurate theoretical methods and the experimental data.

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ELECTRONIC RESONANCES WITH BOUND STATES METHODS AND SOFTWARE

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Keywords : resonances, CAP, MRPT, EOM-CCSD

Abstract: This work will present the recent developments in extending bound state methods and software to describing electronic resonances. We will present an OpenCAP package [1] that allows one to compute resonance parameters (energies and width) by delegating electronic structure calculation to commonly used quantum chemistry packages operating with bound electronic states and integrating the complex absorbing potential at the post-processing stage using projected CAP formalism [2,3]. We will discuss performance of various electronic structure methods (EOM-CCSD, MRPT2, MR-CISD, TDDFT) and their limitations in describing resonance energies and widths for a set of representative shape resonances.

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THE CONSTRUCTION OF A MULTIPOLAR, POLARISABLE FORCE FIELD BASED ON GAUSSIAN PROCESS REGRESSION AND QUANTUM TOPOLOGICAL ATOMS

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Keywords : force field design, machine learning, quantum chemical topology (QCT), QTAIM, active learning, FFLUX

Abstract: We pioneered[1] the use of Gaussian Process Regression (which we regrettably called "kriging" with hindsight) in the design of atomic potentials. Contrary to efforts of other research groups, we started with the machine learning (ML) of accurate electrostatics first, for example, for all 20 amino acids[2]. It is manifest to work with multipole moments if only nuclear sites are used. Next followed accurate ML predictions of the atomic energies. At the heart of this method are quantum topological atoms[3], such that a *single* partitioning provides *all* atomic properties. This approach[4] is now called FFLUX.

Sustained in-house software development led to the ML training program ICHOR and the molecular dynamics program DL_FFLUX, which is an offspring of DL_POLY. Adaptive sampling (which the establishment calls active learning) combined with a AIMD-based sample set produces models with few training point than neural network for small molecules[5]. Improved training now tackles molecules (e.g. paracetamol) up to ~30 atoms (to be published). The recent parallellisation[6] of DL_FFLUX enables the simulation of condensed matter, whether molecular crystals or liquid water (both to be published), all with high-rank polarisable electrostatics. The next major step will be to link models in order to describe oligopeptides and later even proteins.

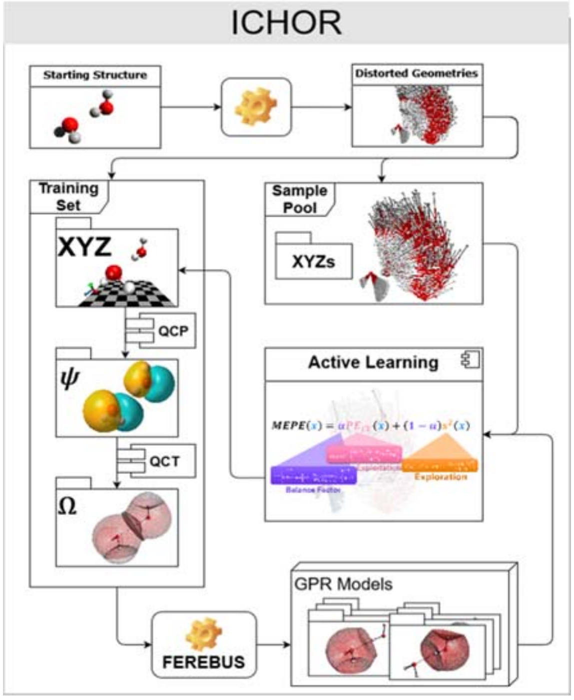

Figure 1: Flowchart of FFLUX's training

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Symposium-2: Modeling and simulation of Low-dimensional systems

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Some recent advances in 2D materials and surface science seen through ab initio calculations

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Abstract:

In the field of nanosciences, research on materials has made spectacular progress over the last twenty years. In this talk, I will present, through some examples from recent works, how ab initio calculations can provide a better understanding of the physical and chemical properties of different compounds. In particular, I will discuss our recent works [1,2, 3] on the properties of indium and gallium chalcogenides 2D systems interfaced with other bidimensional systems such as graphene, blue-phosphorene, or Bi2Se3. Then I will present our recent results [4] concerning the electronic structure of systems consisting of different halogen atoms adsorbed on Cu (111) and Cu (110) surfaces. Our results are compared with ARPES and STS experiments and an excellent agreement between theory and experiment was found. Finally, some current limits as well as future challenges for ab initio calculations will be described briefly.

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AN HR-XRAY INVESTIGATION OF GaAs LAYER GROWN BY MOLECULAR BEAM EPITAXY ON POROUS SILICON MONOLAYERS AND MULTILAYERS SUBSTRATE

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Heteroepitaxy of high quality III-V semiconductor materials (GaAs) on silicon (Si) substrates requires an alternative technique which can eliminate the limitation of lattice mismatch (~ 4 %) [1]. This paper presents a systematic investigation of compliant substrate preparing by an electrochemical etching of Si in an HF solution. Then a thermal annealing was carried out in an Argon gas flow (900°C) for 30 minutes, which launches the reorganization process: in monolayer samples, the pores on the top surface were quietly minimized. However, cavities were increased in the bulk which can be explained by the sintering theory. Regarding multilayers, the low-porosity layer changes into a defect-free crystalline layer, whereas, the highest porosity stack had a microstructural modification explained by the vacancy gradient.

Strain and lattice mismatch were studied in monolayers and multilayers structures by high-resolution X-ray diffraction (HRXRD) and Nano Raman Spectroscopy (NRS). Structure, size and shape of pores were morphologically exanimated via Field emission scanning electron microscopy (FE-SEM). We found that, at constant porosity, strain in both structures were increased with thicknesses and emphasized more under heat treatment. A grown of 500 nm thick GaAs layer by Molecular Beam Epitaxy (MBE) growth technique on these structures using SiGe buffer layer was also studied.

The HRXRD demonstrates that monocrystalline GaAs deposed on multilayers porous structures are more suitable than GaAs grown on monolayers porous silicon structures. However, it appears that the annealed structures prevent the GaAs ‘‘monocrystallization’’.

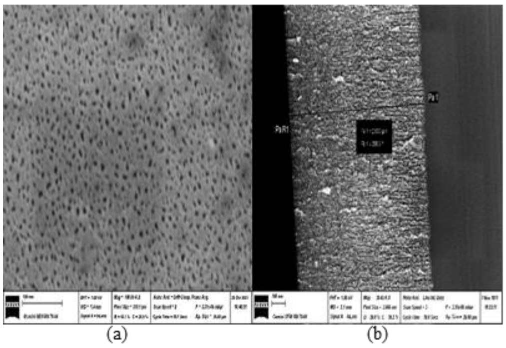

Figure 1: SEM image of multilayer structure: (a) top surface, (b) cross section.

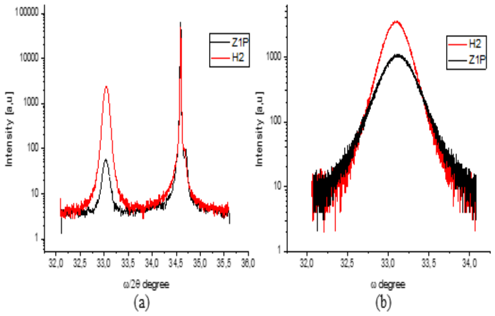

Figure 2: The analysis of crystal quality in the GaAs/SiGe porous structures around (004): (a) coupled scans, (b) rocking curve scans.

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MODELING AND INTERPRETATION BASED ON STATISTICAL PHYSICS TREATMENT OF GRAM-NEGATIVE BACTERIA ADSORPTION ONTO NANOSTRUCTURED SILICON CARBIDE

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In this study, steric and energetic characterizations are determined for the adsorption of gram negative bacteria onto nanostructured silicon carbide using a proposed model expression established by methods of statistical physics to analyze the adsorption mechanism [1].

Firstly, the monolayer model expression with one independent site (Hill model) with three parameters n, Q_{sat} and $C_{1/2}$ is selected as the best fitting model of the experimental data of adsorption of bacteria on silicon carbide nanofibers (NFSiC) and silicon carbide nanorode (NFSiC). The triple-layer model with three parameters n, N_M and $C_{1/2}$ is selected as an adequate model which presents a good correlation with the experimental data of the adsorption of the bacteria on the micrometric silicon carbide (µmSiC). These stereographic and energetic parameters of these physico-chemical models can applied for the characterization of the interactions between the gram-negative bacteria and the nanostructured silicon carbide by calculating adsorption energy values. The results show that the adsorption of bacteria depends on the pH of the medium, the morphology and the texture of silicon carbide.

Secondly, the thermodynamic functions such as entropy, Gibbs free enthalpy and internal energy are investigated and their negative values explain that the adsorption process of bacteria onto nanostructured silicon carbide was exothermic and spontaneous.

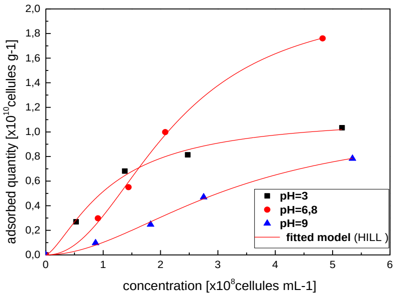

Figure 1: Experimental data of adsorption of gram negative bacteria onto silicon carbide nanofiber (symbols) fitted with a monolayer model with one independent site (line).

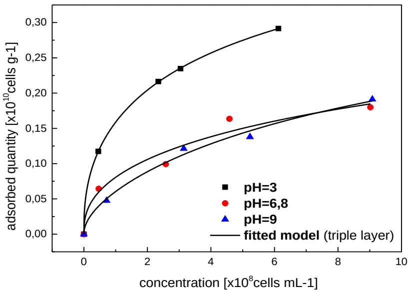

Figure 2: Experimental data of adsorption of gram negative bacteria onto silicon carbide nanorode (symbols) fitted with a triple layer model with one independent site (line).

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CURRENT OVERVIEW OF VICINAL SURFACES: THEORY CONFRONTS EXPERIMENT

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Keywords: vicinal, 1D spinless fermions, terrace-width distribution (TWD), generalized Wigner surmise (GWS), entropic repulsion

Abstract: Study of vicinal surfaces was motivated technologically by their use as growth templates for electronic devices: the terraces between steps have few and minor defects in the direction parallel to the steps. Furthermore, the kinks along a steps are often effective catalytic sites. Vicinals can also provide a way to sort chiral molecules.

The density ρ of steps (and their mean separation $\langle \ell \rangle$, the only characteristic length) of a vicinal surface is determined by the miscut angle ϕ. from a facet-plane terrace. Steps are usually not straight; they meander via kinks due to thermal fluctuations. Opposing this meandering is an entropic repulsion (since steps cannot cross) as well as another repulsion due to stress dipoles. While both decay as ℓ^{-2}, they do not simply add. We use the dimensionless spacing $s \doteq \ell/\langle \ell \rangle$ and write the total step repulsion as g/s^2.

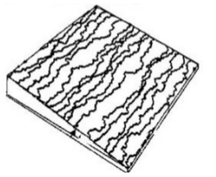

Figure 1: Schematic of a vicinal surface in equilibrium. The tilt angle ϕ is indicated; $\langle \ell \rangle \propto 1/\tan \phi$. Fluctuations of ℓ are evident.

Viewed from above, the equilibrium configurations of these steps fluctuating in 2D correspond to the world lines of spinless fermions in (1+1)D. Thus, the distribution of terraces widths ℓ) between adjacent steps perpendicular to their mean direction, along $\mathbf{e}_x$) corresponds to the distribution of instantaneous separations of the 1D fermions, collected over quantum time. The particle mass is essentially the stiffness of the steps, determined by the kink energy (energy cost of a unit deviation of a step along $\mathbf{e}_x$); the kinetic energy corresponds to the entropic repulsion. In mean field, the single-particle distribution can be found from the Schrödinger equation for a particle in a box or in a harmonic potential well (for no or strong elastic repulsions, respectively).

More generally, the system can be mapped to the venerable Calogero-Sutherland model of repelling fermions on a ring or line, which is exactly solvable for the "inverse temperatures" β = 1, 2, 4, with β simply related to g. The particle separations amazingly correspond to the energy spacings in the Wigner-Dyson model, and the TWD can be well approximated by the Wigner surmise form, with a rise s^β and a gaussian decay in s. Since physical values of g are unlikely to correspond to the special values of $g = 0, 2$, we have used the Wigner expression for arbitrary non-negative values of g. Comparison with Monte Carlo simulations and more importantly with experimental data—from Univ Maryland, FZ-Jülich, and several other leading institutions—for various crystalline samples confirm that this approach captures the essential physics of the problems and provides the best way to extract g from data, the only way for weak elastic repulsion. Several subtleties in confronting experiments with theory will be discussed if time allows.

In recent years, use of deliberately curved crystals has allowed investigation of a range of miscuts—in addition to a standard temperature ramp—in a single experiment. Thereby one find the dependence of electronic states on ϕ [3] and can map out the T- ρ phase diagram for crystals that allow step doubling. Elsewhere, the theory of tuning of topological surface states on topological crystalline insulators (e.g. the tin telluride family) has been formulated [4] but awaits experimental confirmation.

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MOLECULAR STRUCTURE, ELECTRONIC PROPERTIES AND ACETYLECHOLINESTERASE INHIBATION OF A CHOMENE DERIVATIVE

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Keywords : DFT calculations, Chromene Derivative, Molecular docking, Alzheimer's disease.

Abstract:

In this work, structural, electronic and vibrational analyses of a chromene derivative, entitled 2-Amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile and abbreviated as Chrom-D were reported. The FT-IR, UV-Vis and 1H NMR and 13C NMR chemical shifts measurements were recorded [1]. The molecular geometry and the vibrational frequencies are computed in the frame of density functional theory (DFT). The non-covalent interactions responsible to the 3D crystal structure of Chrom-D are investigated based on Hirshfeld surfaces and topological reduced density gradient analysis [2]. Molecular electrostatic potential surface, Mulliken charges and Fukui functions are computed in order to determine the electrophilic and nucleophilic attacks. The electronic properties of Chrom-D are investigated by performing TD-DFT calculations. Finally, molecular docking analysis was performed to study the inhibitor activity of Chrom-D against Alzheimer disease (AD) [3, 4].

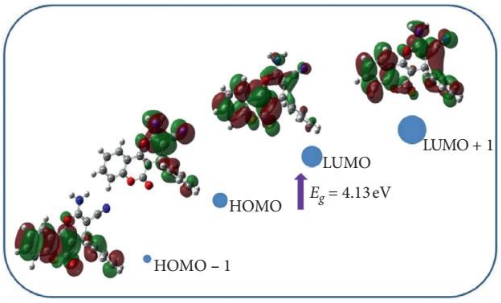

Figure 1: HOMO and LUMO frontier orbitals of the Chrom-D

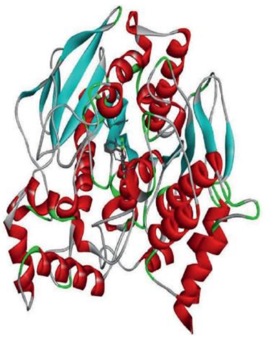

Figure 2: Best pose of the Chrom-D ligand in 1EVE AChE enzyme

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THERMODYNAMIC ANALYSIS OF COOLING CYLES BASED ON STATISTICAL PHYSICS MODELLING OF ETHANOL ADSORPTION ISOTHERMS

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Keywords: Adsorption, Cooling cycle, Isothermic transformation, Isobaric transformation, Statistical physics, Coefficient of performance

Abstract: Thermodynamic analysis of two different adsorption cooling cycles was presented; the first cycle is based on an isobaric adsorption process and the second one projects an isothermal adsorption instead of an isobaric adsorption. These cooling cycles are carried out by employing the grand canonical ensemble of the statistical physics formalism. This investigation is done for two different adsorbate/adsorbent pairs i.e. Ethanol/Waste Palm Trunk (WPT-AC) and Ethanol/Mangrove wood (M-AC). The corresponding adsorption isotherms have been fitted by statistical physics models to give a description of the adsorption process through interpretations of the evolution of the involved physico-chemical parameters, specific for this process. The results showed that the ethanol molecules have been mainly adsorbed with a multimolecular process and non-parallel to the adsorbent surface involving an aggregation process before molecules adsorption. Their adsorption energies are varying from 1.40 to 3.64 kJ/mol for WPT-AC and from 3.2 to 3.81 kJ/mol for the M-AC. These values reflected a physisorption process. The calculated internal energy values suggested the exothermicity and the spontaneity of the ethanol adsorption process. The investigation aims providing a methodology of calculation of the COP for an adsorption cooling cycle by using the statistical physics treatment. The entropy and the enthalpy functions are calculated and used to perform the thermodynamic evaluation and to calculate the coefficient of performance (COP). This parameter was found to be in the interval [0.12–0.69] for ethanol/WPT-AC and [0.11-0.6] for ethanol/M-AC for the first cycle and for the second cycle [0.15-0.81] and [0.15-0.74] respectively.

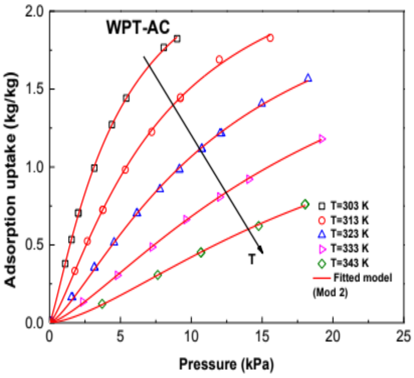

Figure 1: Fitted adsorption isotherms of ethanol on WPT-AC [1]

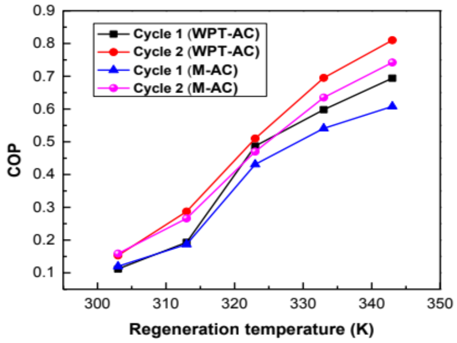

Figure 2: Variation of the COP values.

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INVESTIGATION OF NEW PUSH-PULL CARBAZOLE DERIVATIVES: A COMBINED EXPERIMENTAL AND DFT THEORETICAL INSIGHT

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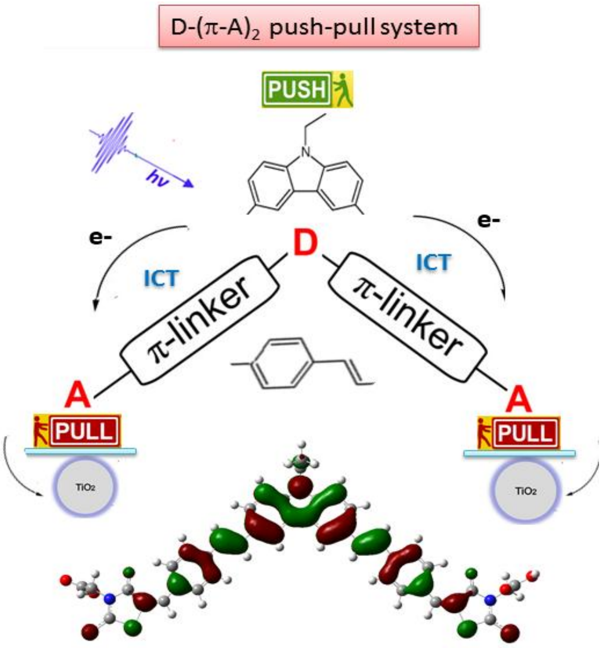
Absract :

New molecularly push-pull organic materials, with predominant intramolecular charge-transfer character, were proposed for dye-sensitized solar cells (DSSCs). The material strucutres are based on a two bromo-distyrylbenzene motives, with N-ethylcarbazole group as a central core, taken as a reference, has been synthesized and characterized. An investigation of absorption UV-vis and emission (PL) behaviour at room temperature was carried. Then, some new classes of carbazole-derived push-pull compounds with variations in their acceptor/anchor groups, containing four different kind electron acceptors (A) and the N-ethylcarbazole group as electron donor (D), denoted as CbzA$_{1\rightarrow4}$ were designed and elucidated. The correlation between structure and opto-electronic properties of these materials has been established. The theoretical investigation of these compounds was performed using DFT and TD-DFT methods, in various solvents of different polarities, to understand their photophysical parameters and electronic properties correlated to their structural features.

The lowest-lying absorption and the fluorescence spectra is the signature of intramolecular charge transfer (ICT) character and founded to be in accordance with experimental values.

Charge transfer parameters, and some reactivity descriptors are calculated and examined.

N-substituted with different chemical groups were also applied to tune and modulate the photophysical properties of these push-pull compounds for good light harvesting and efficient charge transport.



Keywords :

Carbazole, push-pull, free energy, electron injection, charge transfer (ICT), DSSC device.

4-4 Sep 2022

Symposium-1: Novel methodologies for Molecular Electronic Structure

Extending density functional theory with near chemical accuracy beyond pure water

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Keywords : water simulation, density-corrected DFT, dispersion interactions

Abstract: A very recent breakthrough showed that DC-SCAN (the SCAN density functional evaluated on Hartree-Fock densities) yields chemical accuracy for pure water in all its phases [1]. Such a functional could be applied to other liquids and molecules in solution at a fraction of the cost of ab initio quantum chemical methods. But dispersion plays a key role in non-covalent interactions among biomolecules, and its naïve inclusion in DC-SCAN ruins the high accuracy for pure water. Systematic application of the principles of density-corrected DFT yields DC-r^2SCAN-D4, which recovers and improves over DC-SCAN for pure water (Fig. 1) but also captures vital non-covalent interactions in biomolecules.

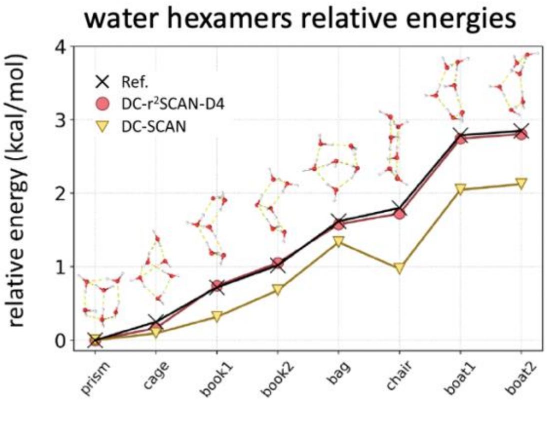

Figure 1: Accuracy of DC-SCAN *vs* DC-r^2SCAN-D4 for water hexamers isomer energies.

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GROUND AND EXCITED STATE ENERGIES IN THE PARTICLE-PARTICLE RANDOM PHASE APPROXIMATION BASED ON THE MCSCF REFERENCE WAVEFUNCTION

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Keywords: RPA, ppRPA, excited states, multireference systems

Abstract: We present preliminary results of a new approach to the computation of the electronic energy of the ground and excited states of an N-electron system, which takes as a reference the wavefunction of an $N-2$ electron system. Our approach is derived from Rowe's equations of motion [1,2] with a particle-particle excitation operator applied to the MCSCF reference wavefunction. The aim of this work is to explore if the ppRPA method improves the accuracy of the MCSCF approach and if it is beneficial to employ the multiconfigurational function instead of a single determinant. We expect our approach to give a good description of double excitations. We present the pilot results for excitation states of a few systems and potential energy curves for several diatomics systems.

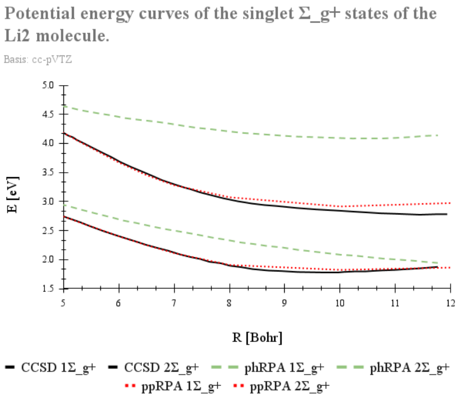

Figure 1: ppRPA based on CAS(4,4) wavefunction vs phRPA/TD-HF. ppRPA employs reduced density matrices computed for Li_2^{2+}.

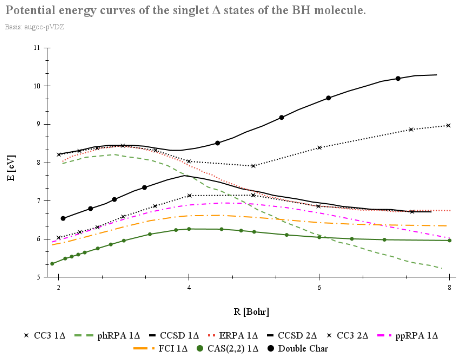

Figure 2: ppRPA based on CAS(2,2) wavefunction vs ERPA and phRPA/TD-HF. ERPA method employs the APSG (antisymmetrized product of strongly orthogonal geminals) reduced density matrices, and ppRPA employs reduced density matrices computed for neutral BH.

Acknowledgment: This work was supported by the National Science Center of Poland under Grant No. 2019/35/B/ST4/01310.

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WAVE FUNCTION BASED QUANTUM EMBEDDING FOR MOLECULES AND SOLIDS

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Wave function based methods are ubiquitous in quantum chemistry, but less often encountered in solid state physics and material sciences, due to their steep computational costs. Instead, methods based on the electron density (DFT) or Green's function (*GW*, DMFT) are predominantly used to simulate extended systems. While these can be accurate, they are often difficult to systematically improve upon.

Here, we present a wave function based quantum embedding approach [1], building on the methods of both density-matrix embedding theory [2] and local coupled-cluster approaches [3], thus bridging the gap between the fields of quantum embedding and quantum chemistry. The approach can readily be applied to both molecular and solid systems and is systematically improvable via a single parameter, determining environment resolution of atomic embedding problems such as the one shown in Fig. 1. Furthermore, the method is computationally efficient, free of empirical parameters, and sidesteps any representability issues encountered in Green's function methods.

An important factor for the accuracy of quantum embedding approaches is the functional with which expectation values are evaluated (see Fig. 2). We will discuss these choices and their consequences and present results for molecular and extended systems in various physical regimes.

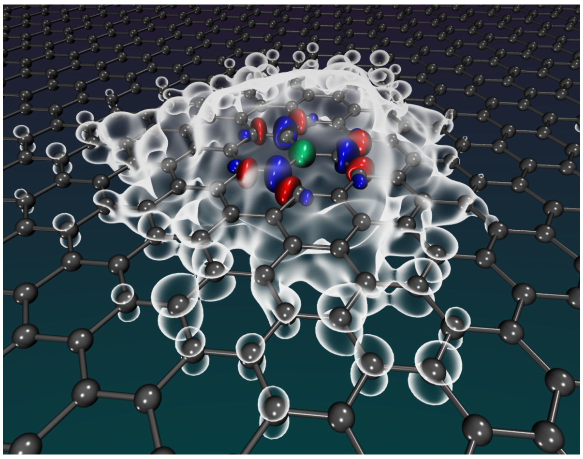

Fig. 1: Embedding of a carbon atom (green) with bath orbitals in a 2D graphene lattice.

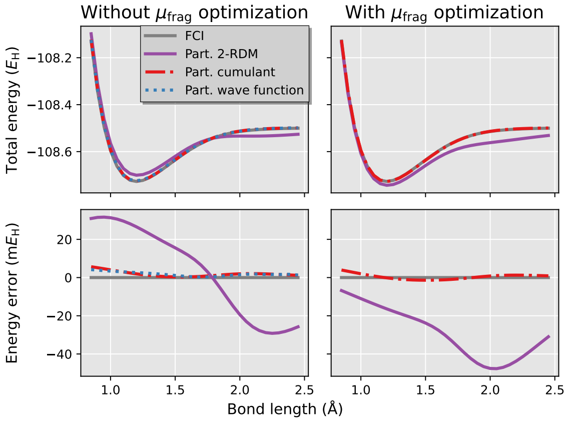

Fig. 2: Comparison of energy functionals used in quantum embedding methods for the dissociation of N_2.

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FLEXIBLE HYBRID FUNCTIONALS FOR THE ELECTRONIC STRUCTURE AT INTERFACES

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Keywords : density functional theory, hybrid exchange functionals, charge transfer at interfaces, dye sensitized solar cells

Abstract:

Density functional theory is the most popular method for electronic structure calculations of molecules and solids. Hybrid exchange-correlation density functionals combine exact exchange with semilocal approximations from Kohn-Sham DFT. While it is possible to describe many basic chemical properties, as well as excitation energies and band gaps accurately with certain types of hybrid functionals, many properties depend crucially on one decisive parameter. This parameter is the percentage of exact exchange in global hybrid functionals or the range-separation parameter in range-separated (RS) hybrid functionals. The latter corresponds to the interelectronic distance at which the functional switches between exact and semilocal exchange.

For a given system it is often possible to determine an optimal parameter, e.g. in optimally tuned RS hybrids. This procedure is however limited in complex systems and when bonds are broken. One example for the former are interfaces between dye molecules and semiconductor surfaces in models for dye sensitized solar cells [1].

In flexible hybrid functionals, that are discussed here, the aforementioned parameters are replaced by a function in real-space. This leads either to local hybrid exchange functionals or exchange functionals with local range-separation. Both functionals can be implemented efficiently[2,3] and improve upon their global counterparts for basic chemical properties. Strategies for the implementation of local hybrid functionals with periodic boundary conditions are presented as well.

Local hybrid functionals are further assessed for the description of level alignments at dye-TiO_2 interfaces in models for dye sensitized solar cells. Several double-donor dyes with a central triphenylamine-unit, that have been investigated previously with standard density functionals and considerably smaller TiO_2-clusters, are considered in this work. Energies of excited states are approximated by linear-response time-dependent DFT and the laser-induced charge-injection is subsequently simulated with the time-dependent configuration interaction methodology.

Our findings confirm a significant dependence of the level alignment at the interface and the degree of hybridization of dye and semiconductor states on the underlying exchange-correlation functional. Consequently, the charge injection may vary qualitatively and quantitatively.

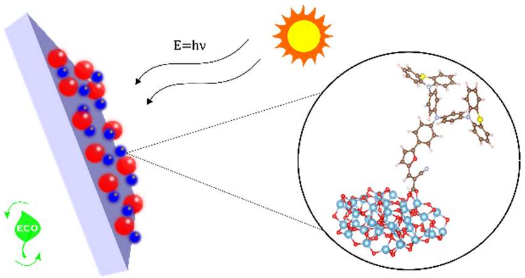

Figure 1: Exemplary dye-TiO_2 system

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MOLECULAR IONIZATION PROCESSES STUDIED WITH CONTINUUM STATES REPRESENTED BY COMPLEX GAUSSIAN-TYPE ORBITALS

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2) LPCT, Université de Lorraine, CNRS, Metz, France

Keywords : continuum states; ionization processes; complex Gaussian-type orbitals

Abstract: The theoretical description of molecular ionization processes requires accurate multicentric wavefunctions. In contrast to bound states, continuum states are generally more difficult to generate numerically, and moreover lead to more elaborate evaluation of those transition integrals needed to get the differential cross-sections.

In a recent paper [1], we have explored the possibility of representing continuum states with real (rGTOs) and complex Gaussian-type orbitals (cGTOs) (see Figure).

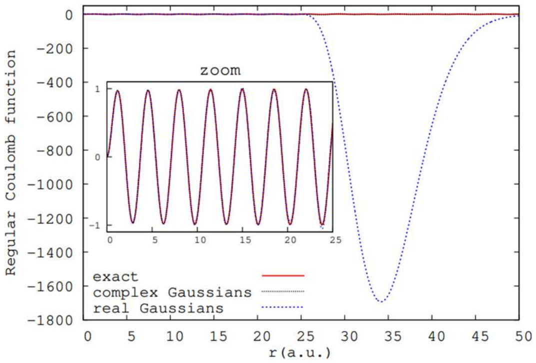

Figure 1: Radial regular Coulomb function (for angular momentum l=1 and momentum k=1.75 a.u.) as a function of the radial distance. Exact function and its rGTO and cGTO representations.

The idea behind this strategy was to exploit the mathematical properties of Gaussian orbitals in order to derive closed form for all the multicenter electronic integrals involved in the calculations. We have shown that extending the domain of definition of the Gaussian exponents to the complex plane addresses the accuracy problem encountered when using nodeless rGTOs to represent oscillating continuum wavefunctions. Accurate one-center calculations illustrated the validity of the proposed analytical approach.

Next, we combined the proposed complex Gaussian representation of the continuum with a real Gaussian expansion for the initial bound state, to implement an all-Gaussian strategy that has then been applied to molecular photoionization [2]. We have optimized sets of complex exponents to cover radial distances up to ~ 30 a.u. and photoelectron energy ~ 2 a.u., and used them to calculate cross sections and asymmetry parameters for NH_3 and H_2O within a monocentric approach. The very good accuracy of the obtained results illustrated the efficiency of the optimized sets. The same strategy was also applied with success to study the ionization of such molecules by electron impact.

To go one step further, we have dropped the monocentric approximation of the initial state. Exploiting again the mathematical properties of Gaussian orbitals, we have shown that also in this case multicenter integrals involving cGTOs can be obtained analytically and evaluated at a significantly reduced cost [3].

Application to ionization cross sections of small molecules will be presented at the conference.

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ANALYTICAL EVALUATION OF HYLLERAAS-CI TWO-CENTER TWO-ELECTRON INTEGRALS OVER SLATER ORBITALS

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It is well-known that atomic and molecular orbitals must decay exponentially at long-range. They should also possess cups when two electrons approach each other. Therefore, Slater orbitals are the natural basis functions in atomic and molecular calculations. While in atomic calculations the use of Slater orbitals is favorable, their use in molecular calculations was hindered by integration problems in the occurring many-center integrals, see review history in [1].

The two-center two-electron integrals have been traditionally the most investigated. There are three types: Coulomb [aa|bb], Hybrid [aa|ab] and the most difficult Exchange [ab|ab] integrals. The classical method of evaluation was the integration in elliptical coordinates [2], which has been recently reinvestigated [3]. Results of integrals calculated with high precision and compared with other methods will be shown [4].

In the more general case, these integrals correspond to the case r_{ij}^{ν} with ν=-1 of correlated two-center integrals. Correlated two-center integrals have been also thoroughly investigated. However, some methods allow the extension to two-center three- and four-electron integrals [5]. One of these methods is based on the modified form of the Neumann expansion [6] by introduction of a set of orthogonal polynomials.

The Hylleraas-CI method has been successfully applied to calculate the ground state of the H_2 molecule [7]. To extend the Hy-CI method to molecules, it is worthwhile to explore new methods of calculation which would be suitable to be extended to the calculation of three- and four-electron two-, three- and four-center integrals.

In this presentation, correlated two-center integrals are calculated with high precision by the integration of the interelectronic coordinate over one of the electrons after a coordinate rotation. We compare these results with the ones using the Neumann expansion. Some preliminary CI calculations on the H_2 and BeH_2 molecules will be also shown [8].

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HIERARCHY CONFIGURATION INTERACTION AND STATE-SPECIFIC APPROACHES FOR EXCITED STATES

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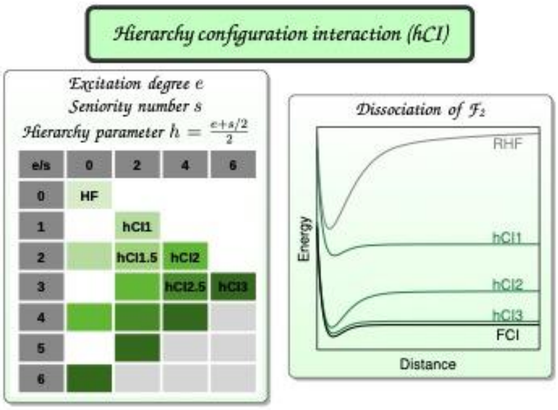
In this talk, I will present some of our recent advances on the selected configuration interaction algorithm named *Configuration Interaction using a Perturbative Selection made Iteratively* (CIPSI) [1,2] to (i) treat weak and strong correlations on an equal footing via a new partitioning of the Hilbert space named hierarchy configuration interaction (hCI) that combines the excitation degree and the seniority number [2], and (ii) compute accurate vertical excitation energies in singly- and doubly-excited states via a state-specific approach.

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481) for funding.



e/s	0	2	4	6
0	HF			
1		hCI1		
2		hCI1.5	hCI2	
3			hCI2.5	hCI3
4				
5				
6				

Figure 1: Hierarchy configuration interaction.

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WHAT IS THE TEMPERATURE OF AN ISOLATED MOLECULE IN A VACUUM?

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Keywords: Microcanonical temperature, spectroscopy, fluorescence, anti-Kasha, PAH, pyrene

Abstract: Defining the temperature of an isolated molecule in a vacuum is helpful for many purposes like understanding radiative cooling, sampling nuclear ensembles, and assigning interstellar molecules. Nevertheless, such a molecular temperature concept has not been well defined so far.

In this lecture, I will discuss how the temperature of an isolated molecule can be derived within the quantum harmonic approximation using statistical thermodynamics. I will examine the effects of the entropy functional choice, evaluate various approximations, and show that we can estimate the molecular temperature as a function of the vibrational energy E_{vib} as [1]

$$T\left(E_{vib}\right)=\left[\ln\left(\frac{E_{vib}+E_{ZP}}{E_{vib}-E_{ZP}}\right)\right]^{-1}\frac{2E_{ZP}}{\left(3N_{at}-6\right)k_B}.$$

where E_{ZP} is the zero-point energy, and N_{at} is the number of atoms (Figure 1).

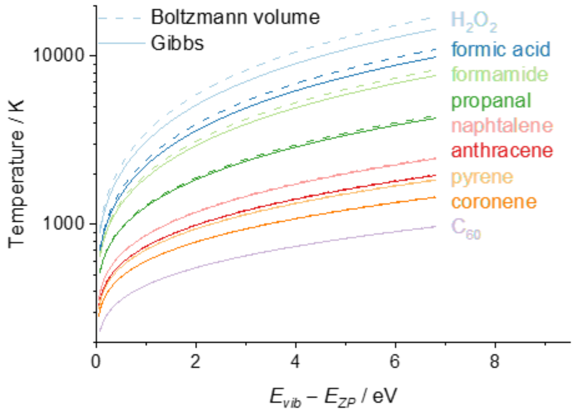

Figure 1: Temperature of isolated molecules as a function of the vibrational energy excess.

This diving into the heart of statistical physics allows us to learn a lot about the thermodynamics of finite systems and even devise an experiment to settle the current debate on which entropy—Boltzmann or Gibbs volume—is the correct one.

I will also show how the direct application of this theory helps assign spectroscopic features in a vacuum and other collisionless regimes. In particular, I will discuss the fluorescence of pyrene [2].

Pyrene fluorescence after a high-energy electronic excitation exhibits a prominent band shoulder not present after a low-energy excitation. The standard assignment of this shoulder as an anti-Kasha emission from the second-excited state (S_2) has been recently questioned. Our results, considering that the excited-state population of pyrene follows a Boltzmann distribution with the microcanonical temperature defined above, confirm that the band shoulder is, in fact, due to S_2 emission.

Nevertheless, we also show that the anti-Kasha behavior requires considerable vibrational energy, which can only be held in collisionless regimes after excitations into highly-excited states. This strict condition explains why the S_2 emission was not observed in some experiments, sparkling the current debate.

Acknowledgments: The author thanks the European Research Council (ERC) advanced grant SubNano (Grant agreement 832237) and the Centre de Calcul Intensif d'Aix-Marseille.

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REDUCTION OF HARTREE-FOCK WAVEFUNCTION TO KOHN-SHAM EFFECTIVE POTENTIALS USING MULTIRESOLUTION ANALYSIS

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We present a highly accurate numerical implementation for computing the Kohn–Sham effective potentials for molecules based on a Hartree–Fock wavefunction and density[1] following the RKS approach of Staroverov and co-workers.[2] Potentials and orbitals are represented in a multiresolution wavelet basis, avoiding basis set incompleteness-related issues. Together with the RKS method, the often occurring problems of oscillating potentials are removed. The MRA implementation of the RKS method allows the generation of molecular Kohn–Sham potentials of benchmark quality. Numerical data for atoms up to Kr and a number of molecules are given, with a special emphasis on the role of nodal planes in the calculations, as showcased in HCN and benzene.

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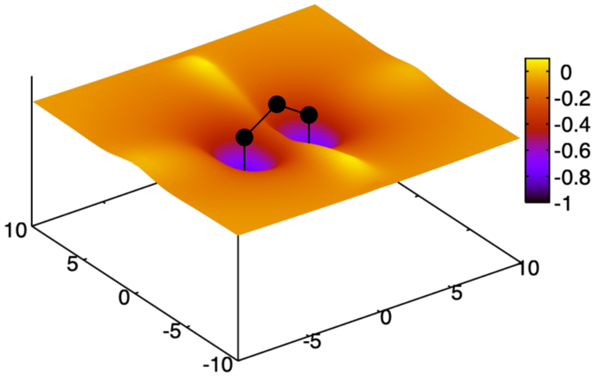

Figure 1: Local exact exchange potentials of the benzene molecule.

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PREDICTION AND ASSIGNMENT OF SPECTRA FROM STRONGLY MAGNETIZED WHITE DWARF STARS USING HIGH-ACCURACY QUANTUM CHEMISTRY

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Keywords : strong magnetic fields, astrochemistry, high-accuracy, coupled-cluster theory, excited states, white dwarf stars

Abstract: Observational spectra from stellar objects allow insight about the composition of their atmospheres. In many cases the recorded spectra can be assigned using accurate experimental data for the species in question. Such assignments, however, become significantly more complicated – or even impossible - when strong magnetic fields are involved. For example, on magnetic White Dwarf (WD) stars magnetic fields of up to about 100 000 Tesla are encountered. On the other hand, on Earth, only up to 100 Tesla can be generated in specialized high-field labs. Hence, predictions can often not be made by experimental means. In such cases, high-level quantum-chemical predictions are essential for the assignment of respective magnetic WD spectra. Because the magnetic and Coulomb forces are equally important, they need to be treated on an equal footing. This is possible when *finite-field* quantum-chemical methods are employed. The development of finite-field Coupled-Cluster[1] (CC) and Equation-of-Motion CC methods[2-5] has enabled such predictions for systems with more than just a couple of electrons. In this contribution we will discuss how respective accurate and reliable predictions are made and present a recent successful assignment of an observational spectrum from a strongly magnetized WD star, through a fruitful interplay between astrophysics and quantum chemistry. The assignment involves the identification of metals in the atmosphere and an estimate of the strength of its magnetic field.[6]

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FULLY AUTOMATIC CALCULATIONS OF ATOMIC ENERGY LEVELS WITH TRUNCATION ENERGY ERRORS

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Keywords: atomic energy levels, correlation energy, optimization of orbital bases with prefixed energy error, selected configuration interaction, truncation energy errors.

Abstract: I discuss approximations to the solutions of Schrödinger's equation for stationary states by means of Configuration Interaction (CI) [1] using (i) optimized orbitals with prefixed energy error PE^{OB} [2], (ii) quickly-evaluated truncated lists of *virtual* symmetry eigenfunctions (SEs) with prefixed energy error PE^{SE}, (iii) the selected SEs evaluated with considerably reduced numbers of orbitals for three- and higher-excited configurations, reflecting improved convergence for high-order excitations, and (iv) selected configuration interaction (SCI) with an additional truncation energy error PE^{CI} [3,4] relative to the Full CI energy.

PE^{OB} is finally replaced by a more reliable energy error ΔE^{OB} based on extrapolations of patterns of energy convergence obtained using *accurate* natural orbitals. The leading part of PE^{SE} is computed by the Brown formula implemented by the formulae developed by the author [3,5] for the coefficients of highly-excited configurations in terms of coefficients of singly-, doubly- and a few triply-excited configurations. The value of PE^{SE} depends on various selection thresholds which are systematically varied until reaching a previously decided acceptable value after a given maximum excitation order n of the CI expansion.

Brown's formula cannot be used *a priori* for linked configurations, *viz.*, those that cannot be decomposed into products of configurations with excitations of lower order. These are efficiently selected by criteria based on products of their corresponding orbital occupation numbers, however, yielding unreliable energy errors thus prompting sensitivity analyses in order to evaluate their energy effect to produce the final truncation energy errors ΔE^{SE} and ΔE^{CI}, respectively. Steps (ii) and (iii) are also used to evaluate approximate natural orbitals from CI wave functions CI-nx up to excitation order n=6.

The novelty I wish to discuss is that the huge number of calculations required above have been concatenated into a single operation carried out by a script written in the old metalanguage bash thus overcoming a very large number of tedious runs prone to innumerable input errors. As an extra bonus, calculations can easily be explained to interested people by varying the all selection thresholds together with examination of sensitivity analyses.

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AN IMPROVEMENT ON THE ILL-CONDITIONED SERIES EXPANSION FORMULAE FOR THE TWO-CENTER CHARGE DENSITY OF NON-INTEGER SLATER-TYPE ORBITALS

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Keywords : exponential type orbitals, Gram Schmidt method, noninteger quantum numbers

Abstract: The complete orthonormal sets of exponential-type orbitals [1] are generalized to non-integer values of principal quantum numbers. This is achieved by performing the Gram-Schmidt procedure [1] for the Slater-type orbitals where the principal quantum numbers are in set of real numbers [3]. A closed form expression for the orthogonalized Slater-type orbitals is achieved. The numerically obtained orthonormal sets of orbitals are generalized to analytical expressions in which the Gram-Schmidt procedure is no loner required. Formulas for the linear combination coefficients are derived. They are used to transform for the complete orthonormal sets of exponential-type orbitals into the Slater-type orbitals (n-STOs). Expansion formulas for the translation of n-STOs are also derived. The n-STOs are expressed in terms of complete orthonormal sets of exponential type orbitals at a displaced center

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SPIN-GENERATOR COORDINATE METHOD FOR STRONG STATIC CORRELATION

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Keywords : electronic structure theory, static correlation, spin symmetry, symmetry breaking,

Abstract: Many of the challenges in popular electronic structure methods for molecules are related to the (de)localization of electrons over the different subsystems in the compounds. We show how incorporating suitable constraints on the quantum many-body wave function can

1. lead to accurate electron (spin)localization in bond dissociation processes [1,2], as described by Yang's flat-plane conditions [3]. This
2. accurately capture static electron correlation via artificial spin-symmetry breaking/restoration [4] in the Generator Coordinate Method (GCM) framework [5].

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Symposium-2: Modeling and simulation of Low-dimensional systems

FIRST PRINCIPLES CALCULATIONS TO INVESTIGATE SPIN-CROSSOVER PHENOMENON IN IRON COMPLEXES

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Spin-crossover has been intensively studied during the last past years due to the need to improve our understanding of the phenomenon and in the hope to exploit switching for data storage at the molecular level. Here we use DFT to calculate and understand the mechanism of spin crossover phenomena [1-4] in $Fe(phen)_2(NCS)_2$ (FePhen) molecule adsorbed on a metallic substrate. We studied the structural, electronic and magnetic properties of the free and adsorbed FePhen molecule on a ferromagnetic metal substrate, such as cobalt, or a paramagnetic substrate such as gold or copper [2-4]. We calculated the energy barrier required for the molecule to switch from low-spin to high-spin states using the "Nudged Elastic Band" (NEB) method. We also computed the ferromagnetic coupling between two magnetic layers, the magnetic FePhen molecule and the cobalt substrate according to the number of non-magnetic intermediate layer of copper [3,4]. The focus is mainly on (1) the role played by van der Waals interactions, (2) the modeling of scanning tunneling microscopy (STM) and (3) the transport properties. We calculated the STM images using the Tersoff-Hamann approximation [2,3], which showed a good agreement with recent experimental STM images.

The triggerable bistability has been used for building devices such as displays and pressure sensors and for certain applications in spintronics and data storage, but the characteristics of the collective spin transition, like being abrupt or smooth, remain difficult to predict since they depend finely on the constituents of the system and their interactions. While numerous experimental and theoretical studies where conducted to gain a better understanding on this family of compounds, most of these studies were performed on mononuclear compounds, but more rarely on binuclear or other more complicated crystal architectures. Here we employ periodic spin polarized DFT+U+D2 calculations, to investigate the structural, electronic and magnetic properties of the tetranuclear $[Fe_4(C_{23}N_6H_{15})_4](BF_4)_4$ molecular crystals [1]. Two geometrical structures of the considered system are evidenced that correspond to two spin state configurations: HS-LS-HS-HS and HS-HS-HS-HS. We found that the two magnetic configurations seen experimentally can indeed by reproduced by our calculations, and that the magnetic centers are coupled ferromagnetically. These findings enable promising electronic and spintronic perspectives.

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OPTICAL PROPERTIES OF TWO-DIMENSIONAL Ti_4GaPbX_2 MATERIALS USING DFT-SIMULATION

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Keywords : two-dimensional, Ti_4GaPbC_2, optical properties …

Abstract

Two-dimensional materials are extensively employed across various investigation areas including photovoltaics, semiconductors, electrodes, and medicine. New progress in top-down and bottom-up synthetic approaches enables the production of 2D crystals with precise and unique optical properties. The optical properties of solids are a significant issue in both fundamental research and industrial employment. Knowing these properties has significant implications both technologically and fundamentally. In this direction, we investigate the optical properties like absorption, conductivity, refractive index, and dielectric function of 2D- Ti_4GaPbX_2 (X = C or N) materials. Our GGA-PBE calculations show that the Ti_4GaPbC_2 monolayer becomes transparent when the frequency of the incident light is higher than the plasma frequency (35.00 eV). However, Ti_4GaPbN_2 becomes transparent when the frequency of the incident light is higher than the plasma frequency ∼ 10.00 eV. Further, we have found that these sheets show a good absorption coefficient in the ∼ 0.00-60.00 eV region.

Moreover, we have found that the conductivity of each compound begins with zero photon energy. Therefore, our 2D materials, *i.e.*, Ti_4GaPbC_2 and Ti_4GaPbN_2 are metal.

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Simulation Monte Carlo du flux de muons atmosphérique au niveau de la mer..

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Les rayons cosmiques sont par définition des particules neutres ou chargées qui atteignent la terre depuis l'espace interstellaire. Lorsque ces particules arrivent sur l'atmosphère terrestre, elles interagissent avec les atomes et les molécules de celle-ci pour produire des particules secondaires formant souvent une gerbe de rayons cosmiques. Certaines particules secondaires produites peuvent arriver jusqu'à la surface de la Terre en traversant plusieurs kilomètres d'atmosphère. Les muons font partie de ces particules et constituent la composante dominante du rayonnement cosmique secondaire chargé au niveau du sol.[1].

La détermination précise de l'angle solide intervenant dans le calcul du flux expérimental de muons [2] est difficile à faire dans la pratique. Ceci est dû à la forme géométrique complexe du dispositif expérimental et la trajectoire des muons qui n'est pas obligatoirement linéaire dans celui-ci (voir Fig.1). Une simulation Monte-Carlo basée sur le logiciel GEANT4 [3] est donc utilisée pour contourner cette difficulté. Elle est basée sur le tirage de nombres aléatoires suivant des lois de probabilité décrivant les processus physiques d'interaction entre les particules générées et le dispositif expérimental.

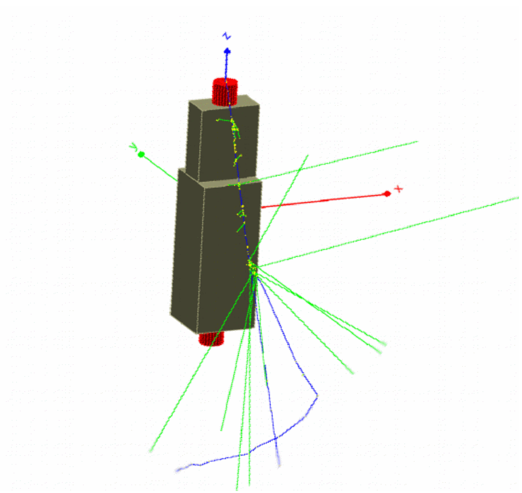

Fig.1 : Dispositif expérimental simulé montrant les deux scintillateurs (en rouge) et les couches de plomb (en gris). Un exemple de muon générée (trajectoire en bleu), interagissant dans le dispositif et donnant naissance à des particules secondaires (en vert), est aussi montré sur la fgure.

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PHYSICO-CHEMICAL CHARACTERIZATION OF THE BINARY MIXTURE OF SUCROSE AND CAFFEINE ON THE β-CYCLODEXTRIN SURFACE BY USING A STATISTICAL PHYSICS MODELING

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Keywords : Sucrose; caffeine; Statistical physics; β-cyclodextrin; PSD and AED.

Abstract: This work represents a contribution in the comprehension of a racimic mixture of caffeine sucrose molecules interaction, by the use of a binary model expression of non-exclusive competitive extended Hill model. This extended model is deduced by statistical physics treatment. The simulation results suggested that the sucrose molecule formed an aggregate of two molecules and linked with a non-parallel position onto the β-cyclodextrin surface. Contrary to the sucrose molecule, the molecule of caffeine, is anchored in a parallel position with the β-cyclodextrin. The adsorption energy distribution (AED) and the pore size distribution (PSD) of β-cyclodextrin are derived through the selected model to describe porosity and energitical in homogeneity of adsorbent surface.

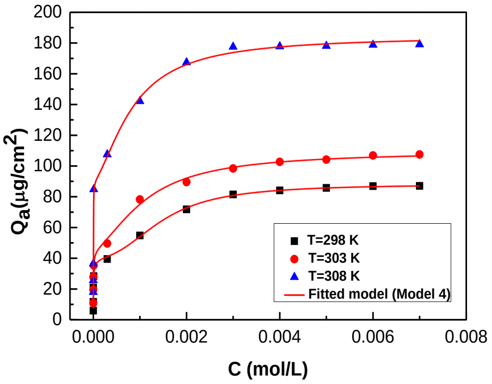

Figure 1: Experimental data of adsorption isotherms of the racemic mixture of Caffeine and Sucrose fitted with the best fitting model

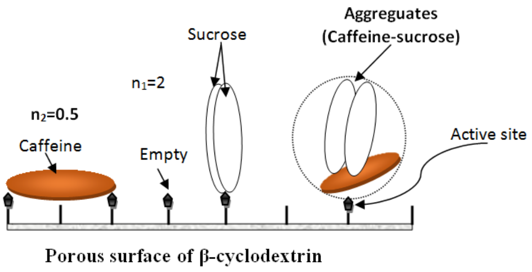

Figure 2: Possible anchorages of the racemic adsorption molecules: sucrose in non parallel position (multimolecular process) (n_1=2) or caffeine in parallel position (n_2= 0.5).

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ELECTRONIC STRUCTURE OF 2D QUATERNARY MATERIALS AND OF THEIR VAN DER WAALS HETEROSTRUCTURES

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Keywords : 2D quaternary compounds, water splitting, Vdw heterostructures

Abstract: The properties of the two dimensional quaternary compounds $AgScP_2Se_6$, $AgBiP_2Se_6$, $CuBiP_2Se_6$, and $CuInP_2S_6$ and the corresponding van der Waals heterostructures are studied using density functional theory. These compounds are dynamically stable, their electronic bandgaps range from 2.13 to 2.68 eV, and the positions of their band edges are suitable for their use for water splitting. Among the different heterostructures made from these monolayers, it is demonstrated that $AgBiP_2Se_6/AgScP_2Se_6$ and $AgBiP_2Se_6/CuBiP_2Se_6$ are type II heterostructures, which allow an efficient electron-hole separation. Then, we studied the electronic properties of the graphene/quaternary-2D-compound heterostructures : a shift of the graphene Dirac-point above the Fermi level is observed, which corresponds to a p-type heterostructure. Overall, this family of materials appears to be very promising for optical and electronic applications.

THEORETICAL INVESTIGATION OF THE Cl_2, *ClO*, AND Cl_2O MOLECULES

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In this work, we investigate the electronic properties of the ground and excited states for Cl_2 and ClO diatomic molecules. These molecular systems received the attention of experimenters and theorists due to their presence in the Stratosphere. To achieve an accurate description, we adopt a theoretical study using numerical simulations with various highly correlated ab initio techniques and basis sets.

We carry out numerous calculations using the MOLPRO software, to solve the Schrödinger equation using the variational principle to approximate the wave functions and the associated eigenvalues, while being in the Born Oppenheimer approximation to treat nuclear and electronic motion separately. Therefore, Hartree-Fock method is always the first prediction, and then we apply various post-Hartree-Fock methods to determine the electronic correlation energies. The objective of our studies is to provide an accurate description for these toxic candidates and to attract and motivate active theoretical and experimental groups worldwide to try to find obvious solutions striving to protect our planet. The potential energy curves are computed for a large and dense grid of internuclear distances. The spectroscopic constants are extracted and compared with previous theoretical and experimental studies. In general, a good agreement is observed with the experimental data **[1]** as well as the theoretical **[2, 3, 4, 5]** results obtained using several techniques such as Interaction Configuration (CI), Multireference Interaction Configuration MRCI with DAVIDSON correction, and Coupled Cluster CCSD(T). Then we extend our study to the ground state of the Cl_2O **[6, 7]** triatomic system. The potential energy surfaces are computed for different angular orientations in the Jacobi frame of reference, using highly performed ab initio methods, MRCI, and MRCI with DAVIDSON and POPLE corrections. As expected, these PESs exhibit a significant anisotropy. These PESs will be used to investigate the transport coefficients of Cl_2 in oxygen gas.

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MOLECULAR DYNAMICS SIMULATIONS OF AQUEOUS KCl SOLUTIONS AT DIFFERENT TEMPERATURES AND SALT CONCENTRATIONS

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Molecular dynamics simulations on potassium chloride solution (2.2 M) at various temperatures (298, 308, 338, and 358K) and at various salt concentrations ranging from 1.55 to 4.27 M (ambient conditions) have been carried out. We chose the flexible SPC water model for the solvent, whereas the ions are treated as charged Lennard-Jones particles. Structural investigations show a decrease of hydrogen bonding as temperature or ion concentration rises, while oxygen-oxygen coordination number increases with increasing temperature and decreases with increasing salt concentration. As mentioned in several earlier studies, our finding shows that the self-diffusion coefficients of ions and water molecules increase with increasing temperatures while their values decrease with increasing salt concentrations. In the temperature and concentration ranges covered in our investigation, The τ_1/τ_2 ratios for the OH vector, show that the reorientational motion of water molecules can be entirely described by an angular jump.

STRUCTURAL INVESTIGATIONS OF LIQUID PROPIONIC ACID BY NEUTRON SCATTERING, DFT CALCULATIONS AND MOLECULAR DYNAMICS SIMULATIONS

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Keywords : Neutron scattering; H-bond; DFT calculation; MD simulations.

Abstract:

Original neutron scattering data on deuterated liquid propionic acid (PA) at large momentum transfer are presented. Experimental data at 298 K and atmospheric pressure in combination with Density Functional Theory (DFT) calculations and Molecular Dynamics (MD) simulations are performed to describe in detail the local order of PA. Neutron scattering data were analyzed to determine the structure factor, the molecular form factor and the intermolecular pair correlation function of the liquid. Some possible molecular arrangements including linear and cyclic dimers and a cyclic trimer, were optimized using DFT calculations to examine their ability to describe the local order of the liquid. MD simulations using the OPLS-AA potential model were performed to describe the experimental data especially at medium and large distances and to highlight the existence of H-bonded clusters in liquid PA.

FIRST-PRINCIPLES CALCULATIONS OF WATER ADSORPTION ON (001) WO_3 SURFACE: DFT AND MOLECULAR DYNAMICS STUDIES

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Keywords: Adsorption, water, WO_3, DFT, molecular dynamics

Abstract: The interfacial properties of water/WO_3 have received particular attention in the theoretical fields, which is relevant for its different applications, particularly for photocatalysis devices. In this work, we aimed at evaluating the hydration mechanisms of the most stable surface of WO_3 and assessing the enthalpies of adsorption of water as a function of the coverage at ambient temperature. Hence, we analyzed the atomistic interfacial properties and their evolution during the gradual hydration of the WO_3 surface, without and with the presence of the implicit solvent, using DFT calculations. The dynamic behavior of the water/WO_3 interface was studied using DFT-based molecular dynamics (DFT-MD) simulations at 300 K, from which theoretical isosteric enthalpies of hydration were calculated, for the gradual hydration of the surface.

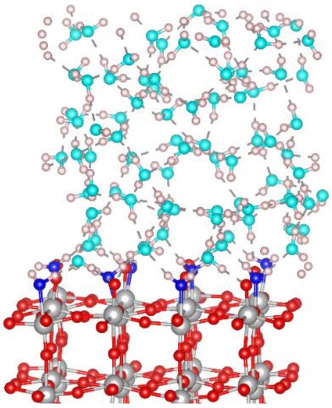

Figure 1. Full hydrated (001) WO_3 surface

Poster

DEVELOPMENT OF THE LENNARD-JONES MODEL WITH NON-EMPIRICAL PHYSICAL PARAMETERS

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Environnement Street, 5019 Monastir, Tunisia

Keywords : Lennard-Jones potential, Harmonic oscillator, rare gas, non-empirical parameters

Abstract:

The aim of this work is to develop a physical methodology leading to obtain a non empirical Lennard Jones model (LJM). Then by expanding the electrostatic potential we will define the constants involved in the LJM. These constants are related to the electric charge, Planck's constant and the vibration frequency. In this treatment we supposed that one atom could be described by a harmonic oscillator. The interaction potential is developed at short and long ranges. The results showed that the obtained physical parameters such as the oscillator frequency, the atom mass, and the atom charge well reproduce the Lennard-Jones potential.

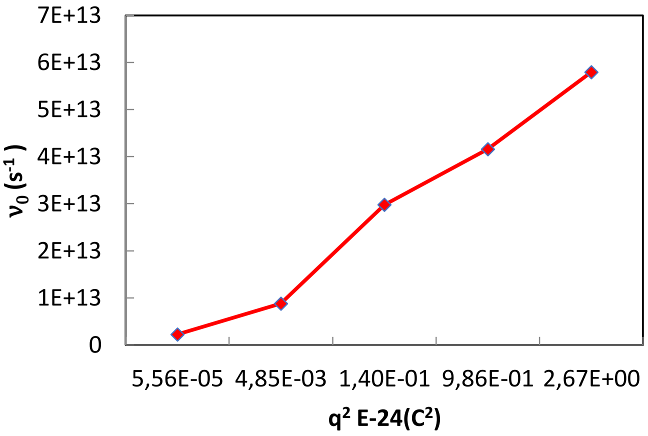

Figure: Evolution of vibration frequency with the square of the atom charge.

DISENTANGLING THE COMPLEX SPECTRUM OF THE ETHYNYL CATION

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Keywords: electronic states, Renner-Teller, vibronic and spin-orbit.

Abstract: Ethynyl cation, C_2H^+ , is of great importance in astrophysical media and in combustion. It is involved in the formation of larger organic compounds and on their decomposition mechanisms. Here, we investigate the low lying electronic states of this cation using pure ab initio methodologies. Evolutions of its potential energy surfaces along the stretching and bending coordinates reveal a high density of electronic states that favours their mutual interactions and the mixing of their wavefunctions. The ground state is of 3 Π space symmetry and the lowest singlet state ($^1\Pi$) is found to be a quasilinear – quasilinear Renner-Teller system. Our work suggests that the (spin-)rovibronic spectrum of such a molecular system is complicated, because of the contributions of multiple couplings, including Renner-Teller, vibronic and spin-orbit. We deduced also the adiabatic ionization energy of the ethynyl radical, in good agreement with recent measurements. In sum, our work shows that the ethynyl cation, in spite of its small size, still represents a challenging molecular problem to be solved [1].

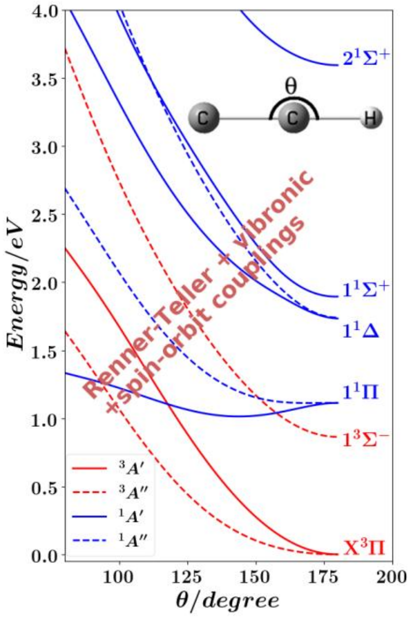

Figure 1: One-dimensional cut of the 3D-PES of C_2H^+ state along the bending coordinate.

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ELECTRONIC STRUCTURE AND PROSPECTS FOR THE FORMATION OF IONIC-MOLECULAR ALKALINE-EARTH-FRANCIUM: ALKE-FR$^+$ (ALKE=BE, MG, CA, SR, AND BA)

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In this work, we report ab initio quantum chemistry calculations on the properties of alkaline-earth-francium Alke-Fr$^+$ (Alke= Be, Mg, Ca, Sr and Ba) molecular ions for their ground and low laying excited states of $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetries. The potential energy curves (PECs) and permanent and transition dipole moments (PDMs and TDMs) are calculated on the basis of non-empirical pseudopotential, core polarization potentials CPP, large Gaussian basis sets and full configuration interaction FCI method. The related spectroscopic constants are extracted using accurate PECs. The results show that, the dissociation energies, equilibrium distances, and PDMs of Alke-Fr$^+$ have an interesting trend depending on the mass of the alkaline-earth-atom **[1-2]**. Stimulated black body (T= 300 K) and spontaneous transition rates are calculated and used to compute radiative lifetimes of vibrational states of the electronic ground states of the Alke-Fr$^+$ molecular ionic systems. Vibrational radiative lifetimes for the first $2^1\Sigma^+$ and second $3^1\Sigma^+$ excited states are calculated and extensively analyzed. Franck–Condon factors are also determined to describe the favorite vibrational transition from the low laying excited $2^1\Sigma^+$ and $1^1\Pi$ states to the ground state $1^1\Sigma^+$. Also, the elastic scattering properties in a range of low energy for Alke-Fr$^+$ are theoretically investigated.

This work provides favorable information for further study of forming ultra-cold molecules via photoassociation technique **[3]**.

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NOVEL POLYCYCLIC SUBSTITUTED PUSH–PULL CHROMOPHORES WITH TUNABLE PHOTOPHYSICAL PROPERTIES: SYNTHESIS, CHARACTERIZATION AND DFT MODELING

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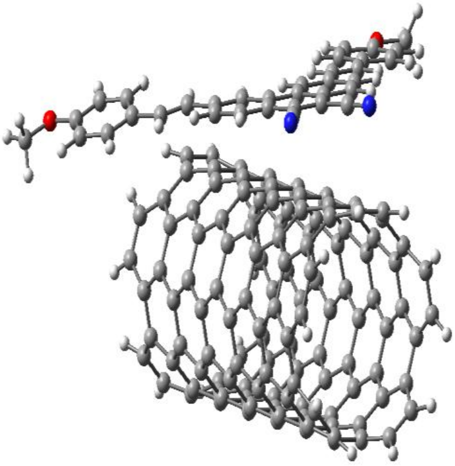
Abstract :

Herein, we present a combined theoretical and experimental study of new push-pull organic chromophores, built as phenanthrene central core with π-conjugating spacers. The photophysical properties of the synthesized compounds have been investigated experimentally using UV-vis, photoluminescence and thermogravimetric analysis. Besides, theoretical geometry optimizations and different simulated spectra were carried out using the Density Functional Theory DFT and TD-DFT calculations showing a full agreement with experimental observations. Overall, a signifcant push–pull character, with intramolecular charge transfer (ICT) states, with donors, accepters and π-conjugates spacers, was elucidated.

The functionalization from noncovalent intramolecular interactions of phenanthrene model compounds with single-wall carbon nanotube (SWCNT) was carried out to examine some fundamental parameters: electric dipole moment (μ), E_{HOMO}, E_{LUMO}, electronegativity (χ), global chemical hardness (η), global softness (σ). Among them, some useful information about the interaction of these push-pull systems with surfaces of SWCNT has been calculated through conceptual DFT. Since, understanding these interactions is crucial for the development of energy storage and conversion systems.

The chromophore is oriented parallel to the SWCNT surface based on optimized π–π interactions where the composite adsorption behaviour is influenced by the chirality and/or the diameter of the SWCNT. The resulting composite turned out to be very efficient charge-transfer chromophores and can be successfully applied in some proposed electronic device. A model band diagram was established simulating the electric response and energy behavior of such electronic device.



Keywords :

Phenanthrene, Push–Pull, DFT, adsorption.

SECOND ORDER COUPLED CLUSTER METHODS FOR ELECTRONIC RESONANCES

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Keywords: electronic resonances; non Hermitian quantum chemistry; complex energy methods; complex absorbing potential; coupled cluster method; photodetachment spectroscopy

Abstract: Electronic resonances are metastable states with finite lifetime. They are encountered in processes such as photodetachment spectroscopy with temporary anions or Auger decay with core-hole states produced by X-rays. The wave function of electronic resonances is coupled to the continuum and hence the resulting energies are observed as increased density of states rather than being discrete [1]. The major problem here is that these states cannot be represented by square integrable wave functions; therefore, they cannot be calculated using electronic structure methods for bound states. The accurate description of metastable states requires the use of complex-energy methods based on non-Hermitian quantum mechanics [2].

In applications to such states, large basis sets with many diffuse basis functions are required. The second order coupled cluster method, CC2 [3], which is an approximation to coupled cluster singles and doubles (CCSD), delivers a good balance between accuracy and computational cost and enables us to study electronic resonances in larger molecules. In the CC2 method, the equation for the determination of the doubles amplitude is approximated by only considering terms up to first order in perturbation theory, whereas the equations for the singles amplitudes stay the same as in CCSD. As a result, CC2 scales only as N^5 with system size. To further optimize the computation, we apply the resolution-of-the-identity (RI) approximation to CC2 [4].

In this project, we introduce the RI-CC2 method combined with various complex-energy methods, complex absorbing potentials (CAP) [5] and complex basis functions (CBF) [6], for the first time. We implemented these methods into Q-Chem electronic structure package [7]. Our focus in this presentation is on the performance of the CAP-RI-CC2 method.

For this purpose, we performed some benchmark calculations on cyanopolyyne anions (C_3N^-, C_5N^-) to compare our method with CAP-EOM-EE-CCSD [8]. These are of interest in astrochemistry as some of the few anions present in interstellar media. The results show that CC2 performs very close to CCSD in accuracy, the difference is ~ 0.4 eV for the resonance energy and ~ 0.1 eV for the resonance width. Complex-energy calculations on electronic resonances are computationally expensive. However, with the CAP-RI-CC2 method, applications to molecules such as citric acid ($C_6H_8O_7$) become possible for the first time. Here, we use CAP-RI-CC2 to study resonances in photodetachment from the dianion of citric acid [9].

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STUDY AND MODELING OF DYE SOLAR CELLS USING STATISTICAL PHYSICS

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Keywords : Dye solar cell, DSSC, Adsorption

Abstract: In this framework, a new digital printing technique for functional materials, called "digital materials deposition (DMD)", developed by the company KELENN Technology, was used to print the different layers of the dye-sensitized solar cell.

First, we are interested in studying the optical properties of the different mesoporous films of TiO2 printed on FTO/glass will be studied by UV-Visible absorption spectroscopy and by photoluminescence at room temperature. Then, a realization and a characterization of device with D35 organic dye, which has a donor-acceptor “push-pull” structure, the study showed that D35 dye is a promising candidate for DSSC applications. Subsequently, we tested the validity of the FTO/TiO2 / D35 system as a sensitized photoanode. The last part of this work discusses the results of electrical characterizations of a DSSC.

This study shows that this new "DMD" printing technology should improve the performance/ efficiency of semi-transparent DSSC cells. Given its undeniable advantages over other technologies, it would be the ideal way to dominate the photovoltaic cell market of tomorrow.

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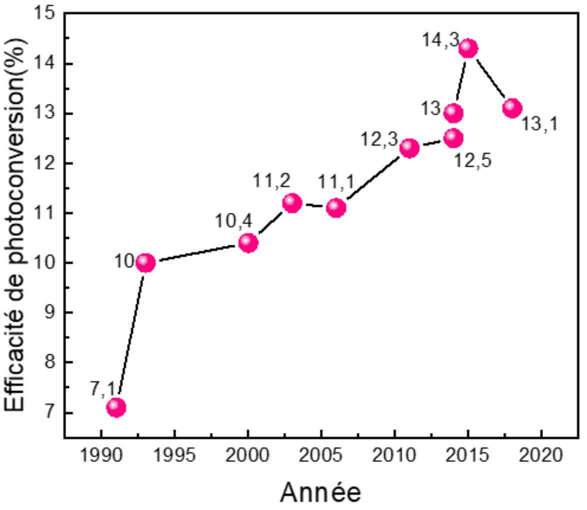

Figure 1: Evolution of DSS conversion efficiencies [1, 2].

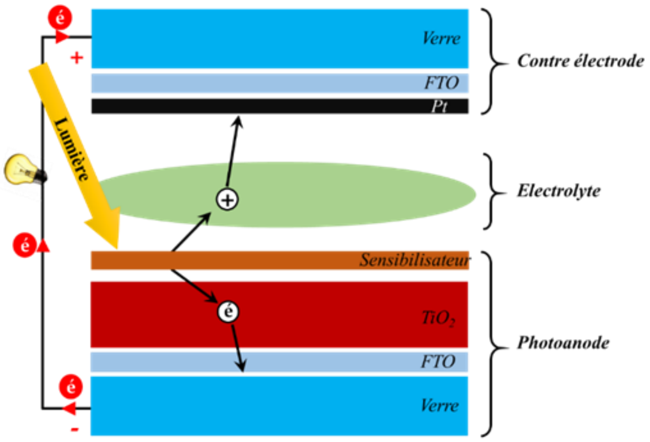

Figure 2: Schematic representation of the components of a DSSC.

Study of structural and optical properties of Cu-Cr substituted Mg-Co spinel ferrites for optoelectronic applications

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Keywords: Spinel Ferrites; Rietveld refinement; Optical band-gap, Refractive index; Urbach energy; Optical conductivity and dielectric constants.

Abstract

The purpose of this work is to study the sintering temperature effects on the structural and optical properties for $Mg_{0.6}Co_{0.2}Cu_{0.2}FeCrO_4$ spinel ferrites. These samples (abbreviated as S900 and S1100) were prepared by sol-gel route and sintered at two different temperatures (900 °C and 1100 °C). Structural analysis by X-ray diffraction technique and structural refinement by Rietveld method confirm the crystallization for S900 and S1100 in the cubic spinel structure. With increasing sintering temperature, unit cell parameters and average crystallites size show an increasing trend. The values of optical band-gap energy (E_g) were calculated using absorbance, reflectance, and Tauc's method. These measurements confirm the direct optical transitions for the prepared samples. The direct band-gap energies for S900 and S1100 were found as E_g= 1.370 eV and E_g= 1.340 eV, respectively. Furthermore, the obtained low Urbach energies (E_u= 0.40 eV for S900 and E_u= 0.33 eV for S1100) confirm the high quality of the prepared sample and imply that the degree of disorder and defects decreases as the sintering temperature rises. The variations with wavelength of optical constants such as penetration depth and extinction coefficient have also been investigated. The Cauchy parameters were estimated from the variation of the refractive index, and the dispersion energy parameters were evaluated from the Wemple–Didomenico relation. The optical conductivity and optical dielectric constants were also analyzed and shown an increasing trend with sintering temperature.

Synthesis, structural, and optical properties for $Ni_{0.4-x}Cu_xCd_{0.3}Co_{0.3}Fe_2O_4$ (x= 0 ; 0.4) spinel ferrites

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Abstract

In this study, we have investigated the effects of the copper substitution on the structural and optical properties for $Ni_{0.4-x}CuxCd_{0.3}Co_{0.3}Fe_2O_4$ (x=0 ; 0,4) spinel ferrites prepared using sol-gel method. According to the Rietveld refinement of the X-ray patterns, the samples were well crystallized in the cubic spinel structure ($Fd\overline{3}m$ space group). Using absorbance, reflectance, and Tauc's method, the values of optical band-gap energies (E_g) were determined. These measurements show that the samples have direct optical transitions. The optical band-gap energies were determined as E_g = 1.24 eV and E_g = 1.14 eV, for x= 0 and x= 0.4, respectively. Additionally, the obtained low Urbach energies (E_u= 1.24 eV for x= 0 and E_u= 1.35 eV for x= 0.4) support a low degree of disorder and defects in the samples. The wavelength variations of optical constants such as penetration depth and extinction coefficient have also been studied. The dispersion energy parameters and the Cauchy parameters were calculated using the refractive index variation and the Wemple-Didomenico relation, respectively.

Keywords : Sol–gel method; $Ni_{0.4-x}CuxCd_{0.3}Co_{0.3}Fe_2O_4$ spinel ferrites; Rietveld refinement; Band-gap energy; Refractive index; Urbach energy.

THE ROLE OF THE HYDROGEN BOND ON THE INTERNAL CONVERSION OF PHOTOEXCITED ADENOSINE

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Keywords : DNA, photophysics, electron-driven proton transfer (EDPT), nonadiabatic dynamics, nucleosides.

Abstract: DNA nucleobases and nucleosides are basic structural units of the building blocks of life, the nucleic acids. They strongly absorb in the ultraviolet region, which could cause substantial photochemical damage to DNA.[1] However, DNA is remarkably photostable thanks to several efficient deactivation processes. In nucleobases, these processes are mainly dominated by internal conversion triggered by conical intersections. [2]

Experiments and theory have revealed that hydrogen bonds can impact and modify the excited-state lifetimes of nucleosides compared to nucleobases. [3-4] Nevertheless, how these HB impact the internal conversion is still unsettled.

In this work, [5] we simulate the nonadiabatic dynamics of adenosine *syn*- and *anti*- conformers in the gas phase using fewest-switches surface hopping approach with ADC(2)/def-SV(P). We considered conformations with and without hydrogen bonds between the sugar and adenine moieties.

The isomer containing the hydrogen bond (*syn)* exhibits a significantly shorter excited-state lifetime than the one without it (*anti*). However, internal conversion through electron-driven proton transfer (EDPT) between sugar and adenine plays only a minor (although non-negligible) role in the photophysics of adenosine.

Either with or without hydrogen bonds, photodeactivation preferentially occurs following the ring puckering pathways. The role of the hydrogen bond is to avoid the sugar rotation relative to adenine, shortening the distance to the ring puckering internal conversion

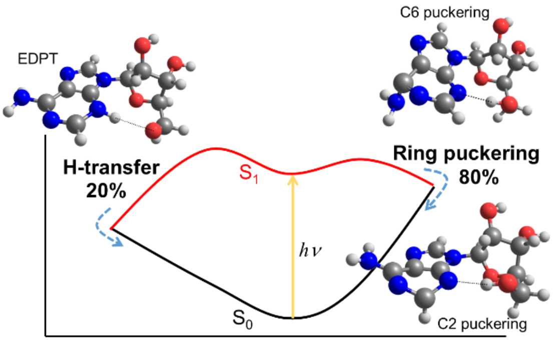

Figure 1: Schematic representation of the decay pathways of *syn*-adenosine.

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5-5 Sep 2022

Symposium-1: Novel methodologies for Molecular Electronic Structure

TOWARDS A BETTER THEORETICAL UNDERSTANDING OF ORGANIC SOLAR CELLS

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After a short review of organic solar cells [1], I will talk about some applied work using the Scharber diagram [7,9] to search for candidate materials [3,5,6]. We will then take a look at fundamental problems, namely the use of density-functional tight-binding (DFTB), density-functional theory (DFT), and the GW method for the calculation of ionization potentials and electron affinities for molecules in organic solar cells [8], the extension of Kasha's model to include charge-transfer excitations [4], and TD-DFTB modelling of the charge-transfer event by fewest-switches surface hopping (FSSH) [2]

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QUANTUM MONTE CARLO STUDY OF SEMICONDUCTOR ARTIFICIAL GRAPHENE QUANTUM DOTS

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Engineering graphene at the nanoscale introduces dramatic changes in the low energy spectrum due to broken sublattice symmetry: a tunable energy gap and magnetic zero-energy modes appear, making graphene nanostructures ideal candidates for nanoelectronic and spintronic applications [1]. However, since natural graphene nanostructures have stability and tunability issues [2], the unconventional electronic, magnetic and optical properties of graphene have not been observed experimentally yet. On the other hand, fabrication of artificial semi-conductor graphene allows better controllability and reliability in terms of structural properties [2,3].

On the other hand, due to their high U/t ratio (see Fig.1 lower panel), artificial graphene nanostructures are expected to exhibit strong correlations effects [4]. Therefore, a rigorous treatment of many-body Hamiltonian is essential for a detailed understanding of electronic and magnetic properties of semiconductor artificial graphene structures.

In this work, we performed variational and diffusion quantum Monte Carlo calculations to accurately take into account strong electron-electron interactions. Many-body trial wave functions were obtained using tight-binding and mean-field Hubbard orbitals, then optimized using a Jastrow factor. The optimized Slater-Jastrow wave functions were used as a guide for the diffusion Monte Carlo calculations within fixed node approximation. This allowed us to accurately investigate the effects of system parameters such as dot radius, potential sharpness, and the distance between dots (see Fig.1 upper panel) and show that a antiferromagnetic-metallic phase transition may occur.

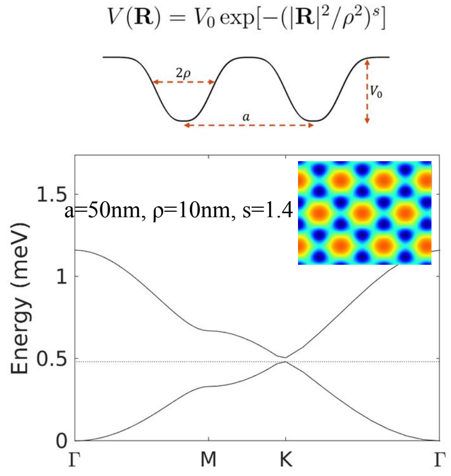

Figure 1: Single particle electronic spectrum of artificial graphene revealing Dirac cones near the K-point with U/t ~ 100.

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FIRST PRINCIPLES MODELING OF MATERIALS AND PROCESSES IN DYE FUNCTIONALISED-METAL OXIDE INTERFACES FOR SOLAR ENERGY CONVERSION

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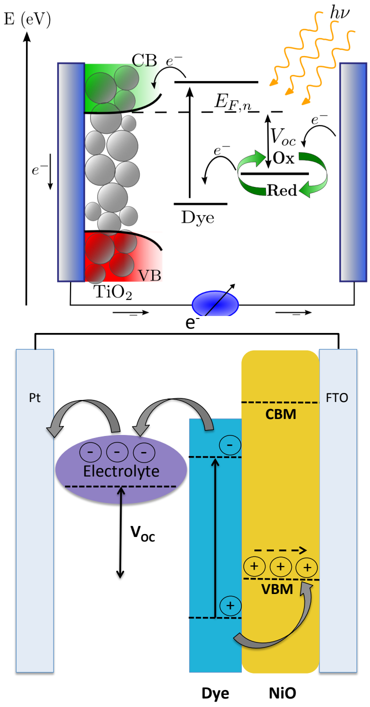

Figure 1. Schematic working mechanism of a n-type (top) an p-type (bottom) photoelectrode

In the context of solar energy exploitation, dye-sensitized solar cells (DSCs)[1] and dye-sensitized photoelectrosynthetic cells (DSPECs)[2] offer the promise of cost effective sunlight conversion and storage, respectively. Dye-functionalization of bot n- and p-type semiconductors (like TiO_2 and NiO, Figure 1, top and bottom panels, respectively) can be either exploited to build active DS photoelectrodes or tandem DSC and DSPECs devices. Computational modelling has played a prominent role in the development of the DSC technology. Here I will discuss the recent advances concerning first principles modeling of materials, interfaces and processes of n- and p-type photoelectrodes. On the photoanode side, we will discuss the recent advances toward the development of more efficient Iron-based DSCs, addressing both the dye design and the electrolyte optimization.[3] On the photocathode side, particular emphasis will be put on the discussion of the electronic and structural properties of the complex NiO/solvent/dye/interface, whose characterization is still poor when compared to the level of understanding reached for TiO_2 sensitized photoanodes, from both the experimental and computational point of view We will discuss the problem of accurately predict the energy level alignment across the dye/semiconductor interface by state of the art DFT and large scale GW calculations and the challenging definition of a proper structural model needed to reliably capture the interface complexity.[4]

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ROVIBRATIONAL ENERGY LEVELS OF MOLECULAR HYDROGEN ISOTOPOLOGUES

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Keywords : hydrogen molecule, rovibrational energy levels, nonadiabatic James-Cooledge wave function, nonadiabatic relativistic correction

Abstract: The total energy and its components for a light molecule can be described in the framework of the nonrelativistic quantum-electrodynamic (NRQED) theory [1] by the following expansion in powers of the fine structure constant

$$E(\alpha) = \sum_{i=2}^{\infty} \alpha^i E^i.$$

Subsequent terms of this expansion are known as the nonrelativistic, relativistic, quantum electrodyna-mic, etc., components of the energy. The higher accuracy is expected, the more components must be involved. Furthermore, the higher accuracy is expected, the more accurate the involved components must be. In particular, the leading term of the above expansion, which represents the nonrelativistic energy, is by far the dominating one and its accuracy can directly limit the accuracy of the total energy $E(\alpha)$. For example, attaining the 1 MHz ($\sim 3\cdot 10^{-5}$ cm^{-1}) accuracy for the dissociation energy of H_2 requires ten significant figures of the nonrelativistic component to be known. A common procedure of decomposing the nonrelativistic energy into the clamped nuclei, adiabatic, and nonadiabatic components can hardly enable such an accuracy. For the four-body systems like the hydrogen molecule, the nonrelativistic energy can also be calculated directly, that is, without expansion in a mass parameter. In the past, such calculations have been performed using nonadiabatic, explicitly correlated Gaussian or Hylleraas functions reaching the accuracy of 10^{-3}-10^{-6} cm^{-1} [2-4]. In this lecture, the results of an approach employing nonadiabatic James-Coolidge basis functions will be presented. This method enables the accuracy of 10^{-7}-10^{-8} cm^{-1} to be obtained for the nonrelativistic dissociation energy of an energy level regardless of its rotational excitation. The newest results for all isotopologues of H_2, including those containing tritium, will be presented and compared with the most recent experimental data. It will be shown that the contemporary theoretical methods and computational techniques allow for accuracy that poses a challenge for the most accurate spectroscopic data [5-9].

Advances in the application of the nonadiabatic James-Coolidge wave functions to the evaluation of the relativistic correction as well as preliminary numerical results will also be reported.

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HARTREE-FOCK CALCULATIONS ON ATOMS WITH COULOMB STURMIAN BASIS SETS

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Keywords : Coulomb Sturmians, Hartree-Fock theory, optimized basis set

Abstract: Effective numerical implementation of the Coulomb Sturmian(CS) basis functions on atoms based on Hartree-Fock theory is presented. Exponential type basis sets are generally preferred for approximating wave functions in numerical electronic structure calculations mainly due to their similarity to the behavior of atomic and molecular orbitals at near and long distances from the nucleus. CSs are particularly beneficial for solving single-particle equations because their screening parameters can be automatically optimized for several orbitals of a given potential. The optimized parameters are obtained from a simple eigensystem constructed by taking advantage of the differential equation that the CSs satisfy. The computational methods in quantum chemistry, such as the Hartree-Fock theory and density functional theory, are based on a one-particle equation with a non-linear potential that is solved by a self-consistent method. This iterative process can benefit from a basis set that remains optimized for all the orbitals that make up the electronic density at every cycle as the effective potential varies until convergence. In this work, the effectiveness of this optimization process is tested on several atoms across the periodic table, where the number of sought atomic orbitals steadily increases. Results indicate that our implementation agrees with the known HF limit total energies and reaches the accuracy of a more time-consuming direct variational optimization of the screening parameters.

ELECTRON-PROPAGATOR, EXTENDED-KOOPMANS AND SELF-CONSISTENT-FIELD PERSPECTIVES ON ELECTRON BINDING ENERGIES

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Three *ab initio* methodologies for the prediction and interpretation of molecular electron binding energies have advanced recently.

1. Electron-propagator (EP) self-energies in the diagonal, or quasiparticle, approximation have been widely used to interpret photo-electron spectra and other ionization experiments for several decades. A new generation of diagonal approximations with superior accuracy and computational efficiency with respect to its numerous antecedents (e.g., OVGF, ADC and G_0W_0 families of methods) has been developed and tested versus a data base of Bartlett and coworkers whose quality approaches that of full-configuration-interaction calculations on vertical ionization energies of representative closed-shell molecules. Subsequent tests on a corrected, symmetry-adapted GW100 data set of molecular and atomic ionization energies demonstrate the superiority of the new methods, which invoke no adjustable parameters in the design of self-energy operators or in the generation of an orbital basis. A non-diagonal EP method with sixth-power arithmetic scaling has error statistics that are comparable to those of the so-called gold standard of quantum chemistry.

2. The extended-Koopmans-theorem (EKT) method often has been employed in the calculation of the lowest electron detachment energy of a molecule or atom where the initial state is represented by a correlated wavefunction or reduced-density matrices. Assumptions that underlie the generalized secular equations of the EKT method have not necessarily been fulfilled in practice. The newly introduced complete-active-space EKT method of Staroverov, Davidson and Ortiz produces electron detachment energies that systematically approach exact results for a given active orbital space with the introduction of basis functions that make much greater contributions to initial, uncharged states than to final, cationic states.

3. Differences in self-consistent-field (SCF) total energies optimized for each state of interest define the ΔSCF method, which has been exploited extensively for core ionization energies by Bagus and others since the 1960s. Two recent theorems by Ortiz and Zalik (OZ) on the eigenvalue spectrum of the difference of two idempotent matrices have revealed how corresponding orbitals derived from SCF wavefunctions determine Dyson orbitals, probability factors, natural ionization orbitals with paired occupation numbers that describe relaxation effects and Fukui functions. The OZ theorems also are applicable to excitation energies, double electron binding energies and any other case in which comparisons between two idempotent density matrices have interpretive value.

6-6 Sep 2022

Symposium-1: Novel methodologies for Molecular Electronic Structure

PROGRESS OF ALGEBRAIC MOLECULAR ORBITAL THEORY

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Our study aims to construct a new MO theory based on algebra as a nonlinear optimization problem of molecular orbital systems with multi-variables. In general, an optimization system consists of an objective function and some constraints functions. In contrast to the traditional MO theory, the new MO theory has two features as follows.

First, the optimization scheme of the traditional MO theory is extended using inequality constraint. The exact solution of the Schrödinger equation satisfies several theorems such as the Hellmann-Feynman theorem and Kato's theorem. We name these theorems Schrödinger constraint collectively. We adopt the inequality constraints which correspond to the Schrödinger constraint in order to approximate the molecular wave function in more close to the exact wave function of the Schrödinger equation.

Second, the new MO system is expressed as a polynomial system consisting of multi-variables such as atomic coordinates and atomic numbers as molecular structure variables, and not only linear expansion coefficients but also orbital exponents of basis functions as variational parameters. This is done by introducing the polynomial expression of molecular integrals obtained by applying the method of Taylor expansion to the analytical expression of molecular integrals with respect to atomic coordinates and orbital exponents. Coefficients of the Taylor series are expressed in rational numbers. We intend to express the new MO system as a polynomial system with just enough accuracy according to the problems. We will present a method of the Taylor series with a given order and a given accuracy in detail and show some examples of polynomial expression of molecular integrals over Slater-type orbitals which are obtained using a symbolic calculation system.

The new MO optimization system is defined as the algebraic system of multivariate polynomial rings which can be operated using computer algebra. It is expected that the nonlinear variational parameters of the orbital exponent and the inequality constraints corresponding to the Schrödinger constraint play a role to yield a more accurate and sensitive approximation over the global region beyond the traditional MO theory. What is more, our study is expected to bring a breakthrough that enables solving inverse problems in quantum chemistry.

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COMPUTATION OF THERMOCHEMICAL PROPERTIES BASED ON INTERNALLY CONTRACTED MULTIREFERENCE COUPLED-CLUSTED METHODS

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High-accuracy computational chemistry provides a powerful tool that can augment the body of experimental data, particularly in case of fleeting intermediates or hazardous compounds. A number of composite schemes have been proposed in the recent decades that aim at the accurate determination of thermochemical properties with sub-chemical accuracy [1-5]. However, most of these protocols defined in this manner are based on single reference methods.

In this study, we evaluate the option of integrating the internally-contracted multireference coupled-cluster (icMRCC) method [6,7] into a high-accuracy thermochemistry protocol. Unlike multireference configuration interaction (MRCI), icMRCC is a size-consistent method and promises uniform accuracy independent of the systems size. The icMRCC approach is a straightforward generalization of the standard coupled-cluster method which bears the option of integrating single-reference and multireference schemes.

In a first step, we evaluate the accuracy of the icMRCC approach, addressing in particular the question how the accuracy of icMRCCSD and icMRCCSD(T) compares to the usual coupled-cluster hierarchy for different cases. We address the question of how certain approximations for the triples approximation [6,7] impact the overall accuracy of the method, in particular if large basis sets are involved. We also investigate the question of choosing active spaces and extrapolating to the complete basis set limit for multireference schemes. Comparison is made to the HEAT protocol for obtaining accurate atomization and reaction energies. We also compare to experimental results from the Active Thermochemical Tables (ATcT). [8]

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COMPUTER-AIDED DESIGN OF ORGANIC MULTIPHOTON ABSORBERS

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Keywords: two-photon absorption; fluorescent dyes; push-pull organic dyes; electronic-structure calculations

Abstract: Technological advances trigger the quest for efficient multiphoton absorbers with tailored photophysical properties. Depending on target application, the absorber must meet several criteria, e.g. absorption wavelength must fit into desired spectral window, multiphoton absorption cross section should exceed required threshold or there should be an efficient emission from electronic excited state. There is an on-going effort to design organic and organometallic systems with significant multiphoton absorption cross sections with an eye towards technology-related applications. The aim of the talk is to demonstrate the usefulness of electronic-structure theories in the design process of efficient multiphoton absorbers, with an emphasis on two-photon absorption. To that end, the underlying theoretical frameworks will be presented and their application to several families of organic absorbers will be discussed based on the analysis of experimental data. The talk will also present the critical assessment of the accuracy of electronic-structure theories and simplified models used in simulations of multiphoton properties.

HARTREE-FOCK-ROOTHAAN THEORY OF MOLECULAR COMPTON PROFILES VIA POSITION SPACE METHOD

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Hartree-Fock-Roothaan theory of molecular Compton profiles has been presented using position space method. Obtained general analytical formula for molecular Compton profiles includes linear combination coefficients of molecular orbitals and molecular Compton profile integrals. Molecular Compton profile integrals have been calculated by integration of molecular overlap integrals times cosine function over range (0,∞). As an application of the presented method in this work, Compton profiles of CO_2 molecule have been calculated over wide range of photon momentum transfer and compared with the available literatüre. It is seen that the obtained results for studied molecule is in good agreement with the literatüre and it is concluded that the presented method is general and can be applied to arbitrary molecule.

UNRAVELLING THE PHOTOPHYSICS OF NATURE-INSPIRED MOLECULAR HEATERS

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Keywords : photophysics, computational chemsitry, excited-states, dynamics, molecular heaters

Abstract: One major challenge in the twenty-first century is to increase global food production while the quality and quantity of arable land are diminishing. Central to this problem is the necessity to increase the yield of numerous important crop species and to find ways to extend geographical locations suitable for agriculture. One environmental constraint which hinders plant growth and development is cold stress.

To protect plants from cold stress, we propose the use of molecular heaters, molecules which could absorb light at specific wavelengths and convert it into heat.

Combining efforts from organic synthesis, spectroscopy, toxicology, and computational chemistry, we present a series of suitable candidates to be used as molecular heaters.[1-3] Particularly, we use different quantum chemical approaches such as TDDFT, DFT/MRCI, CASSCF/CASPT2, and surface hopping simulations to elucidate the photodeactivation mechanism of these molecules.

Our target chromophores are inspired by sinapoyl malate (SM), a naturally occurring molecule identified as an efficient photoprotective plant sunscreen.[4] Our SM derivatives present a fast and efficient relaxation mechanism that involves population transfer from an initially populated bright 1ππ* state to a dark twisted charge transfer (TICT) state. This intermediate state is formed after a carbon-carbon double bond rotation and mediates an efficient internal conversion to the ground state through a conical intersection. The photoisomer formation is naturally prevented due to a symmetric substitution in one of the sp^2 carbons, ensuring almost complete recovery of the initial ground state.

In summary, we present a class of nature-inspired molecules which have an efficient nonradiative energy dissipation mechanism allowing the absorbed light to be converted into heat with minimal implication for photosynthesisthe

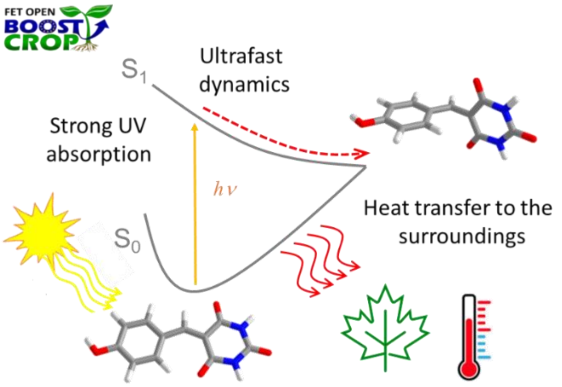

Figure 2: Schematic representation of the photophysics of molecular heaters.

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RECENT DEVELOPMENTS FOR ELECTRONIC RESONANCES: AB INITIO MOLECULAR DYNAMICS, PARTIAL DECAY WIDTHS, AND MORE

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Traditionally, chemistry has focused on processes in which all electrons remain bound to the nuclei. However, state-of-the-art experimental techniques make it possible to create, in a controlled manner, environments where selected electrons are no longer bound to the nuclei. For example, core vacancies produced by X rays, temporary anions obtained by attachment of slow electrons, and molecules exposed to quasistatic laser fields all undergo electronic decay.

The short-lived electronic resonance states that govern electronic decay processes are difficult to model with quantum-chemical methods designed for bound states because these methods do not describe the coupling to the continuum. An elegant treatment of resonances is, however, possible using non-Hermitian quantum chemistry [1]. Complex-variable techniques such as complex scaling, complex basis functions, and complex absorbing potentials (CAPs) describe resonances in terms of discrete states with complex energy and enable the application of concepts from bound-state quantum chemistry (for example, molecular orbitals and potential energy surfaces) to resonances.

In this talk, I will focus on some recent developments in field of non-Hermitian quantum chemistry: In particular, we have devised ab initio molecular dynamics (AIMD) simulations for CAP methods [2]. These AIMD simulations describe nuclear motion on the complex-valued potential energy surfaces of resonance states while taking into account electronic decay at the same time. Applications to the temporary anions of chloroethylene, dichloroethylene, and formic acid illustrate that our CAP-AIMD simulations describe dissociative electron attachment qualitatively correctly already at the Hartree-Fock level.

In addition, I will discuss several ideas for the extraction of partial decay widths from complex-variable calculations, which rely on generalizations of the core-valence separation [3,4]. Exemplary applications to molecular Auger decay (H_2O, CH_4, C_6H_6) and intermolecular Coulombic decay illustrate that complex scaling produces partial decay widths that are in excellent agreement with results obtained using an explicit treatment of the continuum.

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SUMMATION BY EDUCATED MATCH: A POWERFUL TECHNIQUE TO SUM BOTH CONVERGENT AND DIVERGENT SERIES

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Keywords: summability

Abstract: The sum $f(x)$ of a power series, convergent or divergent, is approximated by a linear combination of a scaled, single function $\Phi(x)$ for which the n linear coefficients c_i and the n scaling factors x_i are determined by matching the first $2n$ terms of the power series to be summed.

$$f(x) = \sum_{i=1}^{n} c_i \Phi(x/x_i) + O(x^{2n}) \tag{1}$$

$$f(x) = \sum_{k} f_k x^k \tag{2}$$

$$\Phi(x/x_i) = \sum_{k} \phi_k \; x^k/x_i^k \tag{3}$$

Conceptually, the method rests on the matching of power series of arbitrary functions, not just of the rational functions of the Padé approximants. The power of the method rests on its ability to include information about the sum through the choice of $\Phi(x)$. In practice, however, the $2n$ parameters are calculated using the simple and easily accessible machinery of the Padé approximant.

The quarticly-perturbed harmonic oscillator provides a simple illustration. Its Rayleigh-Schrödinger perturbation theory, a power series in g, the coefficient in the gx^4 anharmonicity, is factorially divergent.

$$E(g) = \frac{1}{2} + g \times \left(\frac{3}{4} - \frac{21}{8}g + \cdots\right) \tag{4}$$

Partial sums beyond $g = 0.1$ are not useful. For large g, the ground state energy goes like $g^{1/3}$, and the series inside the parentheses goes like $g^{-2/3}$, as does the function (for large g)

$$\Phi(g/g_i) \equiv \frac{1}{\Gamma(2/3)} \int_0^\infty t^{-1/3} \frac{e^{-t}}{1 + gt/g_i} dt \tag{5}$$

$$= 1 - \frac{2g}{3g_i} + \frac{10g^2}{9g_i^2} + \cdots \tag{6}$$

The lowest order Φ-approximant,

$$E(g) \approx \frac{1}{2} + \frac{3}{4} g \times \Phi\left(\frac{21g}{4}\right) \tag{7}$$

which uses only the two terms $3/4 - 21g/8$ and the corresponding $1 - 2g/(3g_i)$, tracks the exact energy closely from 0 to ∞.

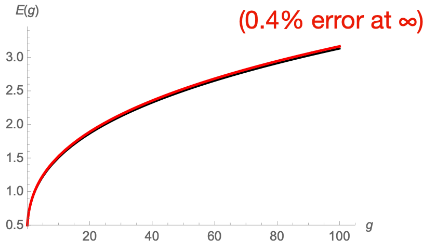

FIG. 1. Φ-approximant (red) vs. exact energy (black).

The Educated Match method generalizes the Padé approximant beyond rational functions and the Borel-Padé method beyond the Borel transform. This presentation generalizes the Educated Match method from divergent power series in Reference [1] to convergent power series.

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QUANTUM MONTE CARLO REACTION BARRIERS FOR DISSOCIATION ON METAL CATALYSTS TO WITHIN 1 KJ/MOL.

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Keywords : Quantum Monte Carlo, solid surfaces, metal catalysts

Abstract:

Selective hydrogen production in mild conditions has now become an important societal goal. Several catalysed reactions have been used and we will discuss water addition to carbon monoxide and direct removal of hydrogen from methane on metal surfaces and films.

The method of choice is Quantum Monte Carlo, which we benchmarked for the activation barrier of our first example (*Phys. Chem. C* 2020, 124, 48, 26232–26240) using a Full CI trial wave-function for the embedded active site, comprising the molecules and surface metal atoms. This was very time-consuming, therefore some tests are in progress with films (so that the active site and film correspond in thickness) as well as several approaches using a ground-state or short CI expansion as trial wave-function and some doped metals with a reduced number of active electrons. The first results show that ground-state input is likely to increase the systematic error to 2-3 kJ/mol for the same example. Doping aluminium, for example, is a promising strategy but complicated to compare with industrial catalysts (see Adv. Q Chem 83 p155 2021).

We have now refined the approach for films of Pt on Al(111) and move towards a second investigation: hydrogen production from methane (leaving coke) on Ni and Pd catalysts. In the example I will show, methane is first adsorbed at Ni (111) and this metal is deposited as a film on gamma Alumina support. Close-packed Nickel is very reactive towards the C-H dissociation process since a Ni-H linkage is formed, offsetting the activation energy. This step is limiting and later products are H_2 and in oxidative systems methanol.

Keywords:

ORCID Number:
0000-0002-2543-5823

References

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Symposium-2: Modeling and simulation of Low-dimensional systems

ELECTRONIC STRUCTURE AND TRANSITION PROPERTIES OF GROUND AND LOW-LYING EXCITED STATES OF BALI$^+$

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Recently, experimental and theoretical techniques have evolved considerably, allowing the characterization and understanding of ion-atom mixtures [1-6]. In this context, we exhibit a theoretical investigation of ground and low-lying excited electronic states of the alkali-metal alkaline-earth diatomic LiBa$^+$ molecular ion.

This study is performed within the ab-initio approach based on non-empirical pseudo-potentials combined with large optimized basis sets for both atoms. In the multireference configuration interaction (MRCI) level of theory, we determined the adiabatic potential energy curves, permanent and transition dipole moments with and without spin-orbit effects for the $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetry. Our results are in good agreement with those of M. Śmiałkowski. and M.Tomza [7].

In addition, spontaneous and stimulated emission calculations and the radiative lifetimes of vibrational states of the ground and the first excited state are determined and analyzed. Moreover, the laser cooling for the BaLi$^+$ molecule feasibility is also discussed.

We hope that the present work stimulates further researchers in the field of ultra-cold quantum dynamics…

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AB INITIO STUDY OF THE IONIC MOLECULE FH$^+$ INTERACTING WITH THE HELIUM ATOM

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We investigate the structure and spectroscopic properties of the ionic molecule FH $^+$ interacting with the helium atom. The calculations were carried out using an ab initio quantum chemistry method. Firstly, we studied the ionic molecule FH $^+$ in its ground state $X^2\Pi$ using several methods of calculation such as MP2, CCSD, CCSD(T), CI and CCSD(T)-F12, with the extended basis sets AVTZ, AVQZ, AV5Z, AV6Z, and cc-pVQZ-F12 and the different extrapolations CBS[TQ5], CBS[Q5] and CBS [56]. We examined the effects of the size of AVNZ-type bases and the CBS[TQ5], CBS[Q5], CBS [56] extrapolations on the minimum energies. Secondly, we investigated the structure and stability of the ionic molecule FH $^+$, taken in its ground state, in interaction with the helium atom, for an extensive range of the remaining Jacobi coordinates, R and θ. For this interaction, the potential energy surfaces are determined using the CCSD(T)-F12 method, and the cc-pVQZ-F12 auxiliary basis set for the hydrogen and fluorine atoms and the basis set cc-pVQZ-F12/optri for the helium atom. A successful agreement is found between our results and those experimental and theoretical available in the literature.

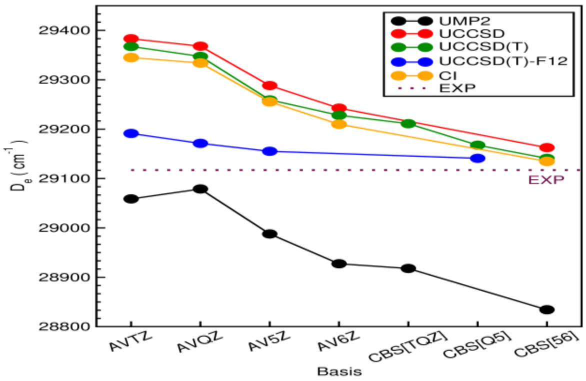

Figure 1: Evolution of the well depth of FH$^+$ in its ground state $X^2\Pi$ function of methods/ (basis and extrapolation).

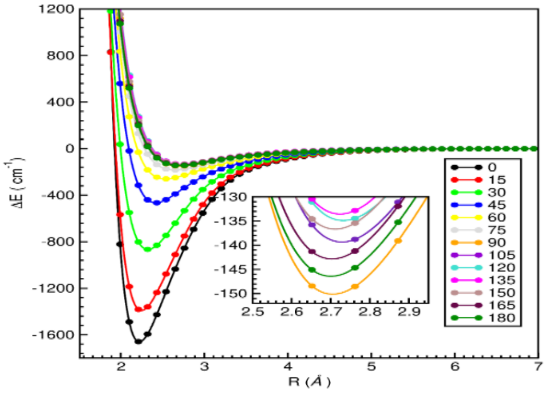

Figure 3: Potential energy surfaces as function of R coordinate of He-FH$^+$.

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SPECTROSCOPIC PROPERTIES AND STRUCTURE OF THE LITHIUM CATION IMMERSED IN SMALL NEON CLUSTERS Ne_N-Li^+(N = 1–20)

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Keywords: clusters; stability; optimization; ab initio; DFT; basin hopping.

Abstract: The geometrical structures and stability of Ne_n-Li^+ clusters with n=1-20, have been investigated using pairwise potentials determined at CCSD (T) level of calculation. The potential energy surface employed in these calculations is based on the Ne-Li^+, Ne-Ne and V_{3B} interactions [1].

For this aim, a series of methods and basis sets have been tested to reproduce accurately the experimental Ne-Li^+ and Ne-Ne potential energies curves.

In addition, both potentials have been fitted by several analytical expressions following Tang and Toennies (TT) [2], Extended Lennard Jones (ELJ) [3] and Lennard-Jones (LJ) [4] formula.

The results show that the most stable structures of Ne_n-Li^+ clusters up to n = 20 have been optimized using the Basin-hopping Monte Carlo method.

Furthermore, these structures are determined through ab initio optimization techniques at CCSD (T) and DFT level of calculations and using Molpro [5] and Gaussian packages.

The relative stabilities of these clusters are discussed by calculating the energy per number of neon atoms, the first derivative and the second derivative of energy to determine the corresponding magic numbers that could be, directly compared with the Mass spectra experimental results.

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DFT COMPLEMENTARY STUDY OF NEW CROSS-LINKED POLYMERS AND COMPOSITES FOR OPTOELECTRONICS

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Keywords : Cross-linking, DFT, Charge transfer.

Abstract: New polymers and organic composites based on bi-carbazole have been synthesized by oxidative route. A cross-linking phenomenon has been appeared (Figure 1) which caused an insolubility problem that prevented to determine the exact chemical structure and also some optoelectronic properties and therefore a misunderstanding of the structure-properties correlation. For this reason, a complementary study using “Density Functional Theory: DFT” has been effectuated, to overcome this lack and to reproduce the experimentally provided properties.

The vibrational and optical parameters of synthesized materials were determined theoretically and compared with experimental ones. To identify the absorption and emission transitions, we calculated the lowest energy levels of the excited states by the TD-DFT method.

The charge transfer between donor and acceptor within polymers and composites was studied experimentally using different experimental analyses in particular optical absorption and photoluminescence and also theoretically by DFT.

All the obtained results support that these new organic materials can be used in the optoelectronic fields due to their original properties.

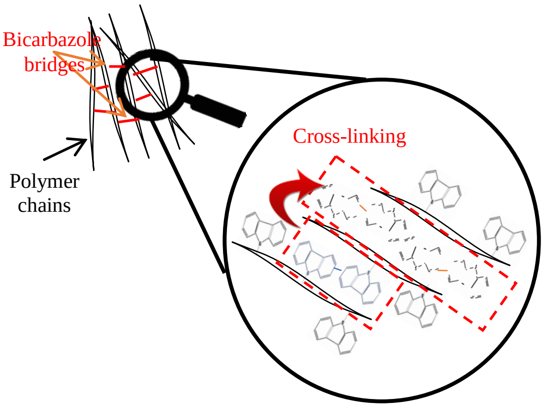

Figure 1: Cross-linking phenomenon

IMPACT OF END GROUP TUNING ON THE ELECTRONIC ENERGY LEVELS AND PHOTO-PHYSICAL PROPERTIES OF IDIC BASED NON FULLERENE ACCEPTORS FOR BULK HETEROJUNCTION ORGANIC SOLAR CELLS : DFT AND TD-DFT STUDY

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Keywords: DFT/TD-DFT; Organic Solar Cell; Intra-molecular Charge Transfer.

Abstract: In order to find novel high-performance non fullerene small molecule acceptors (NFAs) for use in bulk heterojunction organic solar cells, we used density-functional theory and time-dependent density functional theory to design four novel NFAs (M_1-M_4) derived from the recently synthesized IDIC-4CL (M_0). After finding the suitable methods for an appropriate description of the optoelectronic parameters of the reported molecule M_0, we have examined the effect of modifying the electron acceptor terminal of IDIC on their electronic, optical and photovoltaic properties. Different parameters namely HOMO-LUMO gap (E_g) , hardness (η), dipole moment values (μ), exciton binding (E_b), ionization potential (IP), electron affinity (EA), maximum absorption, open circuit voltage (V_{oc}), reorganization energies for holes (λ_h) and electrons (λ_e), were evaluated to predict the relevant candidates for organic solar cell application. Transition density matrix (TDM) and natural bond orbital (NBO) analyses were carried out to further understand the intra-molecular charge transfer between the donor and the acceptor groups. Our calculation predict that M_1-M_4 molecules have not only a low energy gap with a significant λ_{max} in the range of 593-824 nm, low exciton binding, low reorganization energy and significant intra-molecular charge transfer (ICT) properties compared to the reference molecule which suggested that designed molecules may be present suitable candidates for highly efficient solar cells.

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